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A TREATISE

ON

PHYSICAL CHEMISTRY

A Co-operative Effort by a Group of Physical Chemists

EDITED BY

HUGH S. TAYLOR, D.Sc. (Liverpool)

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VOLUME TWO

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". . . There is no branch of work whose constant laws have not close analogy with those which govern every other mode of man's exertion. But more than this, exactly as we reduce to greater simplicity and surety any one group of these practical laws we shall find them passing the mere condition of connexion or analogy, and becoming the actual expression of some ultimate nerve or fibre of the mighty laws which govern the moral world."

RUSKIN—'Seven Lamps of Architecture.'

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CHAPTER XII

THE ELECTROCHEMISTRY OF SOLUTIONS

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The study of the electromotive forces of galvanic cells of various types, which is so fundamental and necessary a part of electrochemistry, is itself to a very large extent a branch of the more general science of thermodynamics. Until it was realized that many of the fundamental phenomena of electrochemistry are subject to the exact methods of thermodynamics, little progress towards a valuable systematization of the subject could be effected.

The application of the exact methods of thermodynamics to this subject began with the studies of Helmholtz [1] and the earlier applications of the equation which relates the electromotive force of a galvanic cell with the internal energy of a chemical reaction and which was derived by Helmholtz.[2] Since the time of these studies, there has been a steady development of the subject which has led to a broader and more accurate knowledge of galvanic electromotive forces and the thermodynamics of solutions. Soon after the investigations of Helmholtz, Jahn and others, Nernst [3] developed his well-known osmotic theory and his formula for the concentration cell. These investigations made possible the definition of the normal electrode potential and gave a great impetus to the further development of the subject. Wilsmore [4] in 1900 compiled a table of standard normal electrode potentials, and in 1911 Abegg, Auerbach and Luther [5] collected all the data available up to that time. In the last decade G. N. Lewis and his colleagues, by employing more exact theoretical methods and attaining greater experimental precision, have increased the accuracy of the values of standard potentials to a very great extent.

The calculation of the variation of galvanic electromotive forces with the pressure, the temperature, and the concentration of the electrolyte, involves the general thermodynamics of solutions. The exact mathematical theory of this subject was first satisfactorily developed in the classic contributions of Gibbs.[6] Gibbs was concerned with fundamental mathematical considerations,

[1] Helmholtz, *Sitzungsber. der Berl. akad.* (1882); Ges. Abl., Bd. II.

[2] Czapski, *Wied. Ann.*, **21**, 203 (1884); Jahn, *Wied. Ann.*, **28**, 21 (1886); **28**, 491 (1886).

[3] *Z. physik. Chem.*, **2**, 613 (1888); **4**, 129 (1889).

[4] *Z. physik. Chem.*, **35**, 291 (1900).

[5] Messungen electromotorischer Krafte galvanischer Ketten, *Abh. Deutschen Bunsen-Gesellschafft.*

[6] *Trans. of Connecticut Academy*, 1875–1878. Scientific Papers of J. Willard Gibbs, Vol. I, Longmans, Green and Co., 1906.

and made no numerical calculations. Even after realization of the importance and usefulness of the "partial quantities" of Gibbs in the thermodynamics of solutions, the difficult task remains of devising methods by means of which partial quantities may be measured and employed in actual numerical calculations. This important step towards the application of the general equations to the specific problems of the physical chemistry of solutions has been carried out with consummate skill by G. N. Lewis [1] and his colleagues. Further, the introduction by Lewis of the activity function has also gone far toward placing the thermodynamics of solutions on a more exact basis, and toward making possible a more exact treatment of the galvanic cell and electrode potentials.

In the following discussion, the thermodynamics of galvanic cells in its relation to the general thermodynamics of aqueous solutions of strong electrolytes will be comprehensively treated. To achieve exactness and eliminate many of the difficulties accompanying the treatment of concentrated solutions, the activity function has been employed. For the sake of uniformity, the same nomenclature and symbols, conventions in regard to sign of electromotive force, etc., as employed by Lewis and Randall have been used. In many sections, the views resulting from recent investigations, although conjectural, are presented with the purpose of introducing the reader to some of the great unsolved problems of the subject, and of indicating the important domains which require much further investigation.

Following the discussion of reversible electromotive forces, and the thermodynamics of solutions of strong electrolytes, an introduction to the phenomena of electrolysis and polarization has been added. This may serve to bridge the gap from the exact study of reversible cells to the extended field of theoretical and applied electrochemistry.

The Galvanic Cell

Whenever two different phases are brought into contact, there may exist between them a difference in electrical potential. The potentials between two solid phases are employed in various kinds of thermocouples. Potentials exist between metals and gases, metals and solutions, at the boundary between two solutions which contain different electrolytes, or the same electrolyte at different concentrations, between a charged particle and the medium in which it is suspended. The cause, the magnitude and the nature of these contact differences of potential are very obscure. Their magnitude is a function of the constitution of the substances, their compositions, their physical states, the temperature, the pressure and obscure surface conditions. The universality of the phenomenon makes the investigation of these potential differences a field of great importance.

The present discussion will be limited to a class of potential differences which are very closely associated with chemical reaction, and the properties of electrolytes in aqueous and non-aqueous solutions. We shall be concerned

[1] Lewis and Randall, Thermodynamics, pp. 617, McGraw-Hill Book Co., New York, (1923).

principally with combinations of three or more contact potential differences at surfaces between metal and solution, gas and solution, metallic solution and solution, two solutions, or metal to metal. Such combinations are designated galvanic cells. The absolute values of contact potential differences are not known. We must, therefore, rest content at the present time to consider them first in combination, and determine their values relative to some standard.

Of all possible combinations of this kind, there are two classes which should be differentiated. There are galvanic cells in which chemical reaction takes place even while no current is passing through the cell. A cell, similar to those constructed by Volta in 1800, and consisting of alternate zinc and copper plates between which was a fibrous material moistened with dilute sulphuric acid, evolves hydrogen when no current is flowing through the cell. Such a cell has but little value in the more exact development of the subject. Then, there is the more important class of cells in which no chemical reaction takes place until a current is caused to flow through them. The Weston cell, in which one electrode is a 12.5 per cent cadmium amalgam in contact with a saturated solution of cadmium sulphate containing crystals of $CdSO_4.\frac{8}{3}H_2O$, and the other electrode is mercury in the presence of solid mercurous sulphate, also in the saturated cadmium sulphate solution, remains in stable equilibrium at 25° [1] when there is no flow of electricity through it. The constancy of the electromotive force of such a cell depends on this stability, and unless the equilibrium in the cell is disturbed by electrolyzing or discharging, and thus producing chemical reactions, the electromotive force will remain constant.

Reversible and Irreversible Cells: A reversible process may be defined as a process of which every state is a condition of stable equilibrium. The evaporation of a given quantity of a liquid at constant temperature and at its vapor pressure, the isothermal expansion of a gas against a pressure exactly equal to the pressure of the gas are reversible processes. The criterion for reversibility is the state of equilibrium, and all measurements of reversible processes depend on the measurement of a system in equilibrium. All actual processes which take place in finite time, or which involve time as a variable, are irreversible.

The criterion of reversibility may now be applied to the galvanic cell.

In the first place, it is obvious that those cells in which there is chemical reaction when no current is flowing cannot be reversible, because an actual process is taking place, and such an unbalanced condition must be irreversible. The Weston cell, on the other hand, may, under certain conditions, be considered as a reversible cell. Imagine the electromotive force of the Weston cell exactly balanced by some outside electromotive force so that no chemical change is produced in it. Then, let this outside electromotive force be increased an infinitesimal amount. Reaction will be started in the Weston cell corresponding to some chemical change, and this reaction will be reversed if the outside electromotive force be diminished an infinitesimal amount. This would be an ideal condition of reversibility, and the exactly balanced state would require an infinitely sensitive galvanometer in the

[1] Recent investigations of Cohen and Moesveld, *Z. physik. Chem.*, **95**, 280 (1920); **104**, 403 (1923), have indicated the presence of a metastable or β modification of cadmium in the 12.5 per cent amalgam at temperatures under 23°, and have shown that the presence of this variety considerably changed the electromotive force of the cell at 0° and other low temperatures.

Weston cell circuit for its measurement. From these considerations, it is clear that any condition involving the passage of a finite current through the cell would be irreversible. In practice, the electromotive force of a cell is always measured by the method of balanced electromotive forces, or the potentiometer method, and the ideal condition, corresponding to reversibility, may be approached as more and more sensitive galvanometers are employed.[1]

Before passing to the consideration of reversible cells and their corresponding reactions, a few further important phenomena should be mentioned. In reversible cells, all substances involved must be in their most stable state. The presence of a metastable modification along with a stable modification of a substance would produce an electromotive force which would not correspond to a reversible process. Further, the potentials of metals depend to a very large extent on the physical structure and state of the metal. Metals in the crystalline form differ from finely divided metals, which are in the more stable physical state. It is well known that the physical state of metals deposited electrolytically is a function of various factors such as the acidity of the plating solution, the current density employed during deposition, and that their potentials with respect to their ions vary accordingly. Aside from these considerations, there are phenomena which occur at boundary surfaces, and which influence the contact potentials. These phenomena, which include overvoltage and passivity, are, for the most part, obscure, but constitute a very important branch of the science of general and technical electrochemistry. We shall reserve the consideration of these and polarization phenomena for a later section, and enter the more exact and fundamental field of reversible electromotive forces.

Reversible Cells and Chemical Reaction: It is important at this juncture to adopt a definite number of conventions for the designation of cells and the sign of electromotive force. The Weston cell will serve as an illustration, and will be written

$$\text{Cd (12.5 per cent amalg.)} \,|\, \text{CdSO}_4.\tfrac{8}{3}\text{H}_2\text{O} \,|\, \text{CdSO}_4 \text{ (sat)} \,|\, \text{Hg}_2\text{SO}_4 \,|\, \text{Hg}; \quad \mathbf{E}_{25} = 1.01810,$$

where $\mathbf{E}_{25}$ denotes its electromotive force at 25° C. The vertical lines serve to divide the phases. When not evident, the nature of the phase, whether solid or liquid, will be denoted by (*s*) and (*l*), respectively. A gas and its pressure will be represented thus: H_2 (1 atm.), Cl_2 (1 atm.). When the phase is a solution, the molal concentration of the solution, expressed in mols (formula weight) in 1,000 grams of solvent, will be given in brackets, and the saturated solution will be designated by (sat). The positive flow of electricity within this cell tends to take place from left to right. The chemical process corresponding to the cell is given by the equation

$$\text{Cd (12.5 per cent amalg.)} + \text{Hg}_2\text{SO}_4 + \tfrac{8}{3}\text{H}_2\text{O} = \text{CdSO}_4.\tfrac{8}{3}\text{H}_2\text{O}\ (s) + 2\text{Hg}; \quad \mathbf{E}_{25} = 1.01810.$$

[1] When measured by the potentiometer method, the electromotive force of a cell is equal to the algebraic sum of the contact differences of potential. We shall refer then to cell electromotive forces, potentials of electrodes in reference to some arbitrary standard electrode, and potential differences at contact surfaces.

That is, the cell does electrical work when the reaction proceeds from left to right. The electromotive force, expressed in volts, will be taken as positive in the direction of the flow of positive current within the cell, or when negative flow is from right to left. The above electromotive force of the Weston cell will be employed as the standard.

When the electromotive force, **E**, is expressed in volts, it equals the electrical work in joules corresponding to the passage of one coulomb through the cell. If, in the cell reaction, **N** gram equivalents are changed, the total electrical work, corresponding to the passage of **NF** coulombs, will be **NEF**, where **F** is the Faraday, or 96,494 coulombs. Since the electromotive force of such a cell is measured under conditions which approach very closely true equilibrium states, **NEF** will be the reversible electrical work of the cell reaction in joules. In the above cell reaction, the value of **N** is 2.

Now, it is possible, by constructing different combinations, to obtain the reversible electrical work corresponding to the various types of chemical reactions. The common general classes are combination, displacement, oxidation, metathesis, and neutralization, and their corresponding reverse reactions.

The reaction of the cell

$$\mathrm{Pt}\,|\,\mathrm{H_2}\ (1\ \mathrm{atm.})\,|\,\mathrm{HCl}\ (0.1)\,|\,\mathrm{Cl_2}\ (1\ \mathrm{atm.})\,|\,\mathrm{Pt};\quad \mathbf{E}_{25} = 1.4885$$

is

$$\tfrac{1}{2}\mathrm{H_2}\ (g) + \tfrac{1}{2}\mathrm{Cl_2}\ (g) = \mathrm{HCl}\ (0.1),$$

which is illustrative of combination.

Many cells have been measured in which the chemical process is a displacement. These may be of various types, of which the Weston cell is a rather complicated example. A simpler cell [1] is

$$\mathrm{Pt}\,|\,\mathrm{H_2}\ (1\ \mathrm{atm.})\,|\,\mathrm{HCl}\ (0.1)\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag};\quad \mathbf{E}_{25} = 0.3522$$

and the corresponding cell reaction is

$$\tfrac{1}{2}\mathrm{H_2}\ (1\ \mathrm{atm.}) + \mathrm{AgCl}\ (s) = \mathrm{Ag} + \mathrm{HCl}\ (0.1).$$

If we had written, for the cell reaction,

$$\mathrm{H_2}\ (1\ \mathrm{atm.}) + 2\mathrm{AgCl} = 2\mathrm{Ag} + 2\mathrm{HCl}\ (0.1),$$

which would correspond to the passage of two Faradays through the cell, the reversible electrical work would have been $2 \times 0.3522 \times 96{,}494$ or 67,972 joules.

Another important type of cell representing a displacement reaction is the Daniell cell, or

$$\mathrm{Zn}\,|\,\mathrm{ZnSO_4}\ (1\mathrm{M})\,||\,\mathrm{CuSO_4}\ (1\mathrm{M})\,|\,\mathrm{Cu}.$$

The cell reaction in this case is

$$\mathrm{Zn} + \mathrm{CuSO_4}\ (1\mathrm{M}) = \mathrm{ZnSO_4}\ (1\mathrm{M}) + \mathrm{Cu}.$$

[1] Noyes and Ellis, *J. Am. Chem. Soc.*, 39, 2532 (1917).

Actually, in this cell, there will be a junction between the zinc and copper sulphate solutions, and, at this boundary, there will be a potential difference which must be eliminated by some method before the potential of the cell reaction can be known. The elimination of this "liquid junction potential" from the total electromotive force of a cell will be indicated as above by introducing two vertical lines.

The following is a good example of a cell without a liquid junction in which the cell reaction is an oxidation. The reaction of the cell [1]

$$\mathrm{Hg|HgCl|KCl\ (0.05),\ K_4Fe(CN)_6\ (0.0005),\ K_3Fe(CN)_6\ (0.0005)|Pt};\quad \mathbf{E} = 0.0609$$

is

$$\mathrm{Hg + KCl\ (0.05) + K_3Fe(CN)_6\ (0.0005) = K_4Fe(CN)_6\ (0.0005) + HgCl}\ (s).$$

In this cell, the solution is a mixture of three electrolytes. Commas are used merely for differentiating the electrolytes present. The cell

$$\mathrm{Pt|SnCl_2\ (0.1),\ SnCl_4\ (0.1)||FeCl_2\ (0.1),\ FeCl_3\ (0.1)|Pt}$$

would correspond to the reaction

$$\mathrm{2FeCl_2\ (0.1) + SnCl_4\ (0.1) = SnCl_2\ (0.1) + 2FeCl_3\ (0.1)}.$$

There is no example of a single cell without a liquid junction in which the reaction is a metathesis or double decomposition. However, Brönsted [2] by combining four cells has been able to determine the reversible electrical work of the reactions

$$\mathrm{NaCl}\ (s) + \mathrm{KBr.2H_2O} = \mathrm{KCl}\ (s) + \mathrm{NaBr.2H_2O},$$
$$\mathrm{KCl}\ (s) + \mathrm{NaClO_3}\ (s) = \mathrm{KClO_3}\ (s) + \mathrm{NaCl}\ (s),$$

where the compounds are all in the solid state.

The cell

$$\mathrm{Tl\ (amalg.)\ |TlCNS}\ (s)\mathrm{|KCNS||KCl|TlCl}\ (s)\mathrm{|Tl\ (amalg.)},$$

which contains a liquid junction has been employed by Knüpffer [3] to measure the reversible electrical work of the reaction

$$\mathrm{TlCl}\ (s) + \mathrm{KCNS} = \mathrm{TlCNS}\ (s) + \mathrm{KCl}.$$

Neutralization may be represented by the cell

$$\mathrm{Pt|H_2|OH^-\ (1M)||H^+\ (1M)|H_2|Pt};\quad \mathbf{E}_{25} = 0.8280,$$

which corresponds to the reaction of the neutralization of strong acids and bases or

$$\mathrm{H^+\ (1M) + OH^-\ (1M) = H_2O}\ (l).$$

[1] Linhart, *J. Am. Chem. Soc.*, **39**, 615 (1917).

[2] *Det. Kgl. Danske. Videns. Selskab. Math.-fysis. Medd.*, No. 3 (1917).

[3] *Z. physik. Chem.*, **26**, 255 (1898).

These examples are sufficient to show that the electromotive forces corresponding to all the common types of reactions involving strong electrolytes may be obtained from suitable cells, or by combining the electromotive forces of suitable cells. Since we shall find that the reversible electrical work is a very important chemical quantity, the measurement of electromotive force of reversible cells is a powerful means for investigation of reactions.

It should be emphasized that by far the most important consideration in dealing with galvanic cells is the exact knowledge of the cell reactions. Many errors have been made and many false conclusions drawn from measurements of electromotive forces without this knowledge.

The Fundamental Thermodynamics of the Galvanic Cell

The Thermodynamic Functions: The energy, U, the entropy, S, the work content, A, the heat content, H, and the free energy, F, are employed in general thermodynamics. In dealing with a particular problem of thermodynamics, it is sometimes more convenient to employ one function, sometimes another. The function employed depends on the nature of the constraints (fixed variables) to which the system under consideration is subjected. To avoid any subsequent confusion, it is desirable to discuss briefly these functions, their relation to the galvanic cell, and to introduce some fundamental equations which will be employed in succeeding deductions.

In the first place, the fundamental equation

$$dS = \frac{dU + pdV}{T}, \tag{1}$$

which Planck[1] has employed as a definition of the entropy of a body, will prove to be very convenient for many subsequent derivations. This equation measures the entropy change of a system in terms of its increase in internal energy and the work performed on another system. It defines the entropy of a system when p is the external pressure on the system when the system is in thermal equilibrium with its surroundings, or the pressure of the system, and, consequently, pdV is the work of a reversible process. In all actual or irreversible processes, where p' is the external pressure on the system when it is not in equilibrium with the surroundings,

$$dS > \frac{dU + p'dV}{T}. \tag{2}$$

These two equations express the content of the second law of thermodynamics. In the case in which the system, that is, the body and its surroundings, is isolated, the familiar and very general expression of the second law

$$dS \geqq 0 \tag{3}$$

results. Thus, any irreversible change in an isolated system is accompanied by an increase in entropy of the system, while during any reversible change the variation in entropy is zero.

Consider any system as undergoing a reversible change and let w equal the work which this system is capable of doing during this change. It is an easy matter to imagine such a func-

[1] Planck, Treatise on Thermodynamics, Longmans, Green and Co. (1903). Translated by Ogg, p. 87.

tion that a change in it may be measured by the work done by the reversible process. In this case when the system passes from one state to another, this function, A, will change from a value A_1 to a value A_2, and

$$(A_1 - A_2) = (-\Delta A) = w.^1 \tag{4}$$

When the system does the reversible work, w, there will be a corresponding decrease in the value of A. For this reason, A may be regarded as the work content of the system.

Since w in the present case is the work of a reversible process, it is the maximum work obtainable from the change, and $(-\Delta A)$ will be independent of the path, and depend solely on the initial and final states of the system. The function A, like the energy and the entropy, is a single-valued function and depends solely on the variables of condition of the system. Further, A like U has no absolute value, but is always measured in respect to some normal state, arbitrarily chosen.

Although the above definition of A is general, it is often very convenient to define it by an equation which relates it to the energy and the entropy. Thus

$$A = U - TS. \tag{5}$$

is an analytical definition of A and is perfectly general.[2]

In cell processes, the total reversible work is the sum of the reversible electrical work, **NEF**, and work gained by the expansion of the system under equilibrium conditions. Thus, for example, in the cell reaction at constant temperature and at constant pressure,

$$H_2\ (1\ \text{atm.}) + 2AgCl = 2HCl\ (0.1) + 2Ag,$$

there will be available the electrical work, **NEF**, but, at the same time, there will be a considerable contraction of volume $(-\Delta V)$, due, principally, to the disappearance of a mol of hydrogen. As a result, work corresponding to $p\Delta V$ will be done on the system. The total reversible work, w, will be **NEF** $+ p\Delta V$, where ΔV is the increase in volume.

Now, consider a function, F, which in general may be defined conveniently by the equation

$$F = A + pV, \tag{6}$$

where p is the pressure of the system and V is the total volume. At constant pressure, a finite change in F will be

$$\Delta F = \Delta A + p\Delta V = (-w) + p\Delta V.$$

Substituting in this equation **NEF** $+ p\Delta V$ for w, we find that

$$(-\Delta F) = \textbf{NEF}. \tag{7}$$

In all cell reactions, at constant pressure and temperature, a decrease in F may be obtained by measurement of the reversible electrical work. It is obvious, from the above considerations, that in cases of condensed systems where ΔV is very small, the change in A and the change in F may be nearly identical. Large errors may be made, however, in confusing these functions.

We shall later find it very convenient to employ the equation

$$F = U - TS + pV, \tag{8}$$

which defines the free energy, F.[3]

[1] Δ denotes an increment.

[2] A is the Helmholtz free energy, or the Gibbs ψ function.

[3] This is the Gibbs ζ function.

It is necessary further to consider one other very important function, the heat content, which may be defined by the equation

$$H = U + pV, \tag{9}$$

and which is related to F by

$$F = H - TS, \tag{10}$$

an equation similar to the one relating A and U.[1]

The heat content function is particularly important because in a chemical reaction carried out at constant pressure, ΔH equals the heat absorbed during the process, or the negative of the heat of reaction. According to the first law of thermodynamics,

$$q = \Delta U + p\Delta V,$$

when the work done is entirely caused by a change in volume, and where q is the heat absorbed. From equation (9) at constant pressure, it is seen that

$$\Delta H = \Delta U + p\Delta V.$$

When during a process the system absorbs heat, the heat of reaction has been ordinarily regarded as negative; it is clear therefore that, at constant pressure, ΔH is the negative of the heat of reaction. When ΔV is very small, ΔH and ΔU become nearly identical.

The variation of the heat content increment with the temperature is given by the well-known equation of Kirchhoff,[2]

$$\frac{\partial(\Delta H)}{\partial T} = \Delta C_p, \tag{11}$$

where ΔC_p is the difference between the sum of the heat capacities of the products and the sum of the heat capacities of the reactants at constant pressure.

The Equations of Gibbs and Helmholtz: The very important fundamental relations involving these functions and their temperature coefficients may readily be obtained from the equations which define them.

Thus, by differentiating (5), we obtain

$$dA = dU - TdS - SdT.$$

Substituting the value obtained for TdS from equation (1), we find

$$dA = -SdT - pdV,$$

whence, at constant volume,

$$\left[\frac{\partial A}{\partial T}\right]_v = -S.$$

Substitution for the entropy in equation (5) gives

$$A = U + T\left[\frac{\partial A}{\partial T}\right]_v, \tag{12}$$

which is the important equation of Helmholtz. In precisely the same way, by differentiating (8), and substituting the value of TdS obtained from (1), we obtain

$$dF = -SdT + Vdp, \tag{13}$$

[1] H is the Gibbs χ function.

[2] *Ann. Physik*, (2) 103, 177 (1858).

whence, at constant pressure,

$$\left[\frac{\partial F}{\partial T}\right]_p = -S.$$

Substituting this value in (10), we obtain

$$F = H + T\left[\frac{\partial F}{\partial T}\right]_p, \tag{14}$$

the extremely important fundamental equation of Gibbs.

The functions A, F, U and H do not possess absolute values but are measured in reference to some standard state. If we consider any change in a system which causes a finite variation of these functions, we write the Helmholtz and Gibbs equations

$$\Delta A = \Delta U + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_v, \tag{15}$$

$$\Delta F = \Delta H + T\left[\frac{\partial(\Delta F)}{\partial T}\right]_p. \tag{16}$$

Of these equations, (14) and (16) are the most important and convenient in chemical calculations, since most measurements of chemical processes are carried out at constant pressure and temperature. In the following discussion, the free energy and heat content will be used exclusively. It will be understood, unless specifically mentioned, that we are dealing with processes at constant pressures, and the subscripts of the differential coefficients will be omitted.

Equations (14) and (16) are often employed for the convenience of calculation in the forms

$$\frac{\partial\left(\frac{F}{T}\right)}{\partial T} = -\frac{H}{T^2} \tag{17}$$

and

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = -\frac{\Delta H}{T^2}. \tag{18}$$

These equations along with (14) and (16) permit the important calculations of free energy and free energy increments from thermal data, and heat content from free energy data. Equations (17) and (18) form the basis for the calculation of the change in free energy with the temperature.

The Calculation of Free Energy and Heat Content Increments of Cell Reactions: When equation (16) is employed for the calculation of heat content changes from free energy data, it is customary to obtain the temperature coefficient of the free energy change, ΔF, by plotting ΔF against the temperature. From the slope of this curve at T, the temperature coefficient of the free energy change is read. By substituting this value and ΔF in equation (16), ΔH may readily be calculated. This method is more reliable in most cases than the method of determining the mean temperature coefficient of free energy over a larger temperature range in the neighborhood of T, since very often the free energy-temperature plot has a considerable curvature. By rearranging equation (16) and changing all signs, we obtain

$$(-\Delta H) = (-\Delta F) - T\frac{\partial(-\Delta F)}{\partial T}.$$

According to equation (7), $(-\Delta F)$ equals **NEF**, and, consequently,

$$(-\Delta H) = \mathbf{NEF} - \mathbf{NF}T\frac{\partial \mathbf{E}}{\partial T}. \qquad (19)^1$$

A comparison of values of $(-\Delta H)$ of a few cell reactions determined by measurement of electromotive force and by calorimetric measurement is given in the last two columns of Table I. The column headings make the table self-explanatory.

TABLE I

COMPARISON OF HEAT CONTENT DECREASES OF CELL REACTIONS IN CALORIES DETERMINED BY MEASUREMENTS OF ELECTROMOTIVE FORCE AND BY THERMOCHEMICAL MEASUREMENTS

Cell Reaction	E	$\frac{dE}{dT}$	$(-\Delta H)$ E.M.F.	$(-\Delta H)$ Thermochemical
(1) $Zn + 2AgCl = ZnCl_2$ (0.555M) $+ 2Ag$ (0° C.)	1.015	−0.000402	51989	52046
(2) $Pb + 2AgI = PbI_2 + 2Ag$ (25° C.)	0.21069	−0.000138	11610	11650
(3) $Cd + 2AgCl + 2{\cdot}5H_2O$ $= CdCl_2\ 2.5H_2O + 2Ag$ (25° C.)	0.67531	−0.00065	40030	39530
(4) $Cd + PbCl_2 + 2{\cdot}5H_2O$ $= CdCl_2\ 2{\cdot}5H_2O + Pb$ (25° C.)	0.18801	−0.00048	15250	14650

(1) Jahn, *Wied. Ann.*, **28**, 21 (1886).
(2) Taylor, *J. Am. Chem. Soc.*, **38**, 2295 (1916).
(3), (4) Taylor and Perrott, *J. Am. Chem. Soc.*, **43**, 486 (1921).

In order to compute the heat content decrease accurately by means of the electromotive force method, the temperature coefficients of electromotive force must be obtained with great precision. Indeed, in the reactions in the above table, an error of 0.01 of a millivolt will cause an error of approximately 130 calories.

Equation (18) may be employed for the calculation of a change in heat content from free energy data. The method is well illustrated by a calculation performed by Ellis [2] from electromotive force data of the cell

$$H_2\ (1\ atm.)\,|\,HCl\ (c)\,|\,HgCl\,|\,Hg,$$

[1] In a system containing only liquids, solutions, and solids, $(-\Delta H)$ is nearly equal to $(-\Delta U)$ or the decrease in intrinsic energy. If the temperature coefficient of electromotive force is very small, equation (19) for a condensed system will approach $(-\Delta U) = \mathbf{NEF}$ and, if $(-\Delta U)$ is expressed in calories $\frac{(-\Delta U)}{23{,}074} = E$, which *inexact* expression is known as the Thomson rule.

[2] *J. Am. Chem. Soc.*, **38**, 737 (1916).

which corresponds to the cell reaction

$$H_2 \text{ (1 atm.)} + 2HgCl = 2Hg + 2HCl \text{ } (c).$$

Table II contains some of his electromotive force data.

TABLE II

ELECTROMOTIVE FORCE DATA OF THE CELL: H_2 (1 ATM.)|HCl (c)|HgCl|Hg

c	E.M.F.			$10^6\,\alpha$
	18°	25°	35°	
0.1004	0.39764	0.39884	0.40013	+ 386
0.3376	0.33845	0.33836	0.33794	− 75
0.7714	0.29654	0.29571	0.29411	− 460
4.484	0.15759	0.15506	0.15124	− 2384

The electromotive force **E** at different temperatures may be computed for each temperature by the equation

$$\mathbf{E} = \mathbf{E}_{25}(1 + \alpha(t - 25)),$$

where the values of α are given in the last column of the table. The free energy decrease of the cell reaction as written will equal $2 \times 23{,}074 \times \mathbf{E}$ calories, and also

$$(-\Delta F) = (-\Delta F)_{298}(1 + \alpha(T - 298)).$$

Now, if this value for $(-\Delta F)$ be substituted in (18) and the differentiation performed,

$$(-\Delta H)_{298} = (-\Delta F)_{298}(1 - 298\alpha)$$

is obtained. In Table III, are given values of $(-\Delta F)$ in calories computed from the electromotive forces, and $(-\Delta H)_{298}$ calculated by this last equation.

TABLE III[1]

$(-\Delta F)$ AND $(-\Delta H)_{298}$ OF THE CELL REACTION IN CALORIES

c	$(-\Delta F)_{291}$	$(-\Delta F)_{298}$	$(-\Delta F)_{308}$	$(-\Delta H)_{298}$
0.1004	18351	18407	18466	16290
0.3376	15620	15616	15596	15965
0.7714	13685	13647	13593	15528
4.484	7273	7156	6980	12240

[1] Usually in the text the centigrade temperature scale will be employed. In recording numerical data involving changes in the thermodynamic functions, it is more customary to employ the absolute temperatures.

This method of calculation should be employed when it is possible to express the electromotive forces as a function of the temperatures by a simple equation.

Further Important Properties of the Free Energy: By differentiating (8) at constant temperature and pressure, we obtain

$$[\partial F]_{p,\,T} = dU - TdS + pdV.$$

But according to (1) and (2)

$$TdS \geqq dU + pdV,$$

whence by substitution

$$[\partial F]_{p,\,T} \leqq 0. \tag{20}$$

This equation corresponds to the statement that all actual variations in systems at constant temperature and pressure are accompanied by a decrease in free energy, and that the criterion for stable equilibrium is that the free energy remains unchanged. This very important principle can be clearly understood by further consideration of the cell reactions. When the cell reaction can proceed spontaneously, in a direction corresponding to the direction of the flow of positive electricity in the cell, there will be a decrease in free energy. It is then obvious that, at constant temperature and pressure, a cell reaction can only proceed $\rightarrow$ direction corresponding to a decrease in F, or when $\Delta F < 0$. The sign of the free energy change is thus an exact criterion for predicting the direction of the reaction. The determining factor of stable equilibrium of the cell reaction will then be the condition that at constant temperature and pressure

$$\Delta F = 0. \tag{21}$$

The value of the free energy is thus not only a criterion of equilibrium but also of the stability of systems. For, if we consider the reaction

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl\ (0.1); \qquad \Delta F_{298} = -34{,}346, \qquad \text{or} \qquad (-\Delta F)_{298} = 34{,}346,$$

we find that the change from left to right is accompanied by a very large decrease in free energy. It may be said that the system hydrogen and chlorine gas is very unstable. The decrease in free energy may therefore be considered as a measure of the affinity of a reaction, and in many systems of thermodynamics $(-\Delta F)$ has been denoted the "affinity."

The Concentration Cell without Liquid Junction: Up to the present, only the free energy and heat content changes of cell reactions, which are complete chemical reactions and which do not involve changes in composition of any of the phases, have been discussed. We have now to consider free energy and heat content changes of quite a different nature, and processes in which the compositions of the phases play a predominant rôle.

The electromotive forces of cells, corresponding to the following cell reactions, measured by Linhart,[1] will serve as an illustration:

$$\tfrac{1}{2}H_2\ (1\ \text{atm.}) + AgCl = Ag + HCl\ (0.001);$$
$$E_{25} = 0.5785; \quad (-\Delta F)_{298} = 55{,}822$$

and

$$\tfrac{1}{2}H_2\ (1\ \text{atm.}) + AgCl = Ag + HCl\ (0.0483);$$
$$E_{25} = 0.3870; \quad (-\Delta F)_{298} = 37{,}343.$$

[1] Linhart, *J. Am. Chem. Soc.*, **41**, 1175 (1919).

If the second reaction be subtracted from the first, the result will be

$$\text{HCl (0.0483)} = \text{HCl (0.001)}; \quad \mathbf{E}_{25} = 0.1915; \quad (-\Delta\bar{F})_{298} = 18{,}479.$$

The free energy decrease is in joules. This equation means that the net effect of the two cell reactions is the transfer of a mol of hydrochloric acid from a solution of 0.0483 molal concentration to a solution of 0.001 molal concentration, and that the free energy decrease of such a change is 18,479 joules. In other words, $(-\Delta\bar{F})$ is the free energy decrease when a mol of hydrochloric acid disappears at 0.0483 molal concentration and appears at 0.001 molal concentration. The most important point is that $(-\Delta\bar{F})$ may be regarded as the difference of two quantities, which are the change in free energy, $\bar{F}_2$, when a mol of hydrochloric is added to an infinitely large quantity of 0.0483 molal concentration, and the change in free energy, $\bar{F}_1$, when a mol is added to an infinitely large quantity of solution containing 0.001 molal hydrochloric acid. $\bar{F}_2$ and $\bar{F}_1$[1] will be denoted the partial molal free energies of the hydrochloric acid in the two solutions respectively. It is always the case that the partial free energy is greater in the more concentrated solution, or $\bar{F}_2$ is greater than $\bar{F}_1$. Consider the transfer of a mol from the more concentrated to the more dilute solution. The *removal* of this mol from the concentrated solution will be accompanied by a change in free energy equal to $-\bar{F}_2$, and the addition of this mol to the more dilute solution will be accompanied by a change in free energy $+\bar{F}_1$. The total free energy increment of transfer will be the sum of these quantities, $(\bar{F}_1 - \bar{F}_2)$ or $-(\bar{F}_2 - \bar{F}_1)$, which equals a decrease in free energy $(-\Delta\bar{F})$, and which in turn equals **NEF**.

In a similar manner, by subtracting the values of the heat content changes of the cell reactions computed by the Gibbs-Helmholtz equation (Table III) at two different concentrations, the difference in partial molal heat contents of the acid at the two concentrations may be obtained. From the nature of these processes we are led to the consideration of a whole series of quantities which will prove to be of great importance in the application of thermodynamics to solutions.

These changes in partial molal free energy and heat content could have been obtained directly from measurements of cells of the type

$$\text{Ag}\,|\,\text{AgCl}\,|\,\text{HCl}\ (c_2)\,|\,\text{H}_2\,|\,\text{HCl}\ (c_1)\,|\,\text{AgCl}\,|\,\text{Ag},$$

where the net result of the cell reaction would be the change

$$\text{HCl}\ (c_2) = \text{HCl}\ (c_1).$$

This type of cell will be denoted the concentration cell without liquid junction.

For the measurement of partial free energy changes of electrolytes containing a metal which readily reacts with water, there are available cells in which the metal electrode is a very dilute amalgam. For example, the cell

$$\text{Ag}\,|\,\text{AgCl}\,|\,\text{KCl}\ (c_2)\,|\,\text{K (dil. amalg.)}\,|\,\text{KCl}\ (c_1)\,|\,\text{AgCl}\,|\,\text{Ag}$$

[1] A partial quantity or a change in a partial quantity will always be represented by a dash over the symbol.

affords measurement of the partial free energy change corresponding to the transfer [1]

$$KCl\ (c_2) = KCl\ (c_1).$$

The determination of partial free energy and heat content changes by the electromotive force method may also be applied to the study of solutions of electrolytes in metallic solvents. The electromotive force of the cell at constant pressure and temperature

$$Me\ (c_2)\ (amalg.)\,|\,MeX\ (solution)\,|\,Me\ (c_1)\ (amalg.),$$

consisting of two amalgam electrodes at different concentrations connected by a solution of a salt of the metal, MeX, is independent of the concentration of this salt solution and depends only on the composition of the amalgam. The net effect of the cell reaction is the disappearance of the metal from the amalgam of the higher concentration, and its appearance in an amalgam of lower concentration. This process is accompanied by a decrease in free energy equal to the difference in partial free energies of the metal in the amalgams of the two concentrations, or $-(\bar{F}_2 - \bar{F}_1)$ if c_2 is greater than c_1. A most exhaustive study of the cell

$$Tl\ (c_2)\ (amalg.)\,|\,Tl_2SO_4\,|\,Tl\ (c_1)\ (amalg.)$$

has been carried out by Richards and Daniels,[2] as a result of which the partial free energy and heat content changes of both the thallium and mercury are accurately known.[3] Indeed, the stability of the amalgams permitted measurements to solutions as concentrated as 40 per cent of thallium.

This type of cell has been mentioned to illustrate that electromotive force measurements are of great value in the study of metallic solutions. Since the present discussion is confined particularly to solutions of electrolytes, further discussion of this interesting subject will be omitted.

Partial Molal Quantities

General Considerations: The value of a thermodynamic function, for example, the energy, of a substance in a given state in reference to some standard state is determined by the variables of condition, the pressure, the volume and the temperature. Thus,

$$U = f(p, v, T) + U_0,$$

where U_0 is a normal state, arbitrarily selected. There is always some relation, such as

$$f(p, v, T) = 0,$$

[1] MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915).
[2] *J. Am. Chem. Soc.*, **41**, 1732 (1919)
[3] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 233 (1921).

which is called an equation of state of the substance, and as a result of which one of the variables depends on the other two. It is then possible to evaluate the function by means of any two independent variables. Thus,

$$U = f(v, T) + U_0 = f(p, T) + U_0, \text{ etc.},$$

is true for any simple substance.

A thermodynamic function of a phase composed of two or more components is not determined by two of the above independent variables, but is only determined by two of these variables and the masses of the components. We shall find it most convenient to choose the pressure and temperature as well as the masses as the independent variables. The energy of a given phase may be expressed by

$$U = f(p, T, m_1, m_2, \cdots m_c) + U_0.$$

In like manner the general equation for the free energy of the phase is

$$F = f(p, T, m_1, m_2, \cdots m_c) + F_0,$$

where m_1, m_2, etc., are the masses of the c components of the phase, and F_0 is the free energy of an arbitrarily selected state. If we now consider an infinitesimal change in F and partially differentiate the right-hand member of this equation, we obtain

$$dF = \frac{\partial F}{\partial p}dp + \frac{\partial F}{\partial T}dT + \frac{\partial F}{\partial m_1}dm_1 + \frac{\partial F}{\partial m_2}dm_2 + \cdots \frac{\partial F}{\partial m_c}dm_c.$$

But, according to equation (13),

$$\partial F = -SdT + vdp$$

for a phase, or a system of phases at constant composition, and, therefore,

$$dF = -SdT + vdp + \frac{\partial F}{\partial m_1}dm_1 + \frac{\partial F}{\partial m_2}dm_2 + \cdots \frac{\partial F}{\partial m_c}dm_c. \qquad (22)$$

In general, we shall make these partial derivatives in respect to mass equal to μ_1, μ_2, etc., respectively, according to the notation of Gibbs, and, as a consequence, equation (22) becomes

$$dF = -SdT + vdp + \mu_1 dm_1 + \mu_2 dm_2 + \cdots \mu_c dm_c \qquad (23)$$

and, at constant pressure and temperature,

$$dF = \mu_1 \partial m_1 + \mu_2 \partial m_2 + \cdots \mu_c \partial m_c. \qquad (24)$$

Equation (23), which was originally obtained by Gibbs, and relations immediately deducible from it, may serve as a general fundamental relation underlying the thermodynamics of solutions.[1] This equation is valid for any phase of a c component system. By considering a system of P phases, and by using an

[1] See van der Waals-Kohnstamm, Lehrbuch der Thermodynamik, Vol. II (Maas and van Suchtelen, Amsterdam).

equation similar to this but involving the energy, Gibbs [1] in his famous memoir was able to deduce the phase rule. It should always be borne in mind that equation (23) and similar ones make possible an exact study of systems of many components in one phase, or many phases. In considering complicated chemical systems, there is no safer method than to employ these general equations of Gibbs.[2] An important conclusion for the discussion in hand is the principle, immediately deducible upon application of equation (23) to a system of phases, that when a polycomponent system in p phases is in stable equilibrium, and, if μ_1, μ_1', $\cdots$, μ_1^p represent the μ values of the first component, μ_2, μ_2', $\cdots$, μ_2^p represent the μ values of the second component throughout the p phases, etc., for the c components, then, at constant pressure and temperature,

$$\left.\begin{aligned} \mu_1 = \mu_1' = \mu_1'' \cdots = \mu_1^p, \\ \mu_2 = \mu_2' = \mu_2'' \cdots = \mu_2^p, \text{ etc.} \end{aligned}\right\} \tag{25}$$

It was because of this property of these partial derivatives that Gibbs denoted them the "chemical potentials."

Just as with entropy or energy, the free energy of a homogeneous system is doubled if its mass is doubled. From this property, and from inspection of equation (23), it is clear that μ_1, μ_2, etc., are independent of the masses, and depend only on the composition, or relative quantities of the components, and the units in which the free energy and masses are expressed. As a consequence, equations (23) or (24) may be integrated. Equation (24) thus becomes

$$F = \mu_1 m_1 + \mu_2 m_2 + \cdots + \mu_c m_c. \tag{26}$$

Complete differentiation of this latter equation gives

$$dF = \mu_1 \partial m_1 + m_1 \partial \mu_1 + \mu_2 \partial m_2 + m_2 \partial \mu_2 + \cdots \mu_c \partial m_c + m_c \partial \mu_c. \tag{27}$$

Elimination of dF from (24) and (27) gives the important equation

$$m_1 \partial \mu_1 + m_2 \partial \mu_2 + \cdots m_c \partial \mu_c = 0. \tag{28}$$

We have yet to consider the units in which these quantities may be expressed, and, for the sake of simplicity, let us choose a phase of two components. If (26) is divided by $(m_1 + m_2)$ or the total mass, we obtain

$$\frac{F}{(m_1 + m_2)} = \left(\frac{m_1}{m_1 + m_2}\right)\mu_1 + \left(\frac{m_2}{m_1 + m_2}\right)\mu_2.$$

Thus, if F is the free energy per gram, $\left(\frac{m_1}{m_1 + m_2}\right)$ and $\left(\frac{m_2}{m_1 + m_2}\right)$ are the weight fractions of the components, and μ_1, μ_2 or $\frac{\partial F}{\partial m_1}$, $\frac{\partial F}{\partial m_2}$ may be denoted

[1] Transactions of the Connecticut Academy (1875–1878). Scientific Papers of Willard Gibbs, Vol. 1. Longmans and Co.

[2] Williamson and Morey, *J. Am. Chem. Soc.*, **40**, 49 (1917); Morey and Williamson, *J. Am. Chem. Soc.*, **40**, 59 (1917); Morey, *J. Franklin Inst.*, **194**, 425 (1922).

partial specific free energies. In a similar manner, the free energy per mol of a phase may be defined by $\frac{F}{n_1 + n_2}$, where n_1 and n_2 are the number of mols of each component, respectively. Substituting mols for grams, we obtain according to (26)

$$\frac{F}{n_1 + n_2} = \frac{n_1}{n_1 + n_2}\overline{F}_1 + \frac{n_2}{n_1 + n_2}\overline{F}_2,$$

where μ_1 and μ_2 are now $\overline{F}_1$ and $\overline{F}_2$, the partial molal free energies, and $\frac{n_1}{n_1 + n_2}$ and $\frac{n_2}{n_1 + n_2}$, which we denote N_1 and N_2, are the mol fractions.

Thus, denoting the free energy per mol, F, we may write (26) and (28)

$$F = N_1\overline{F}_1 + N_2\overline{F}_2 + \cdots + N_c\overline{F}_c \tag{29}$$

and

$$o = N_1\partial\overline{F}_1 + N_2\partial\overline{F}_2 + \cdots N_c\partial\overline{F}_c. \tag{30}$$

Now, in the same manner, it is possible to regard many quantities such as the heat content, the volume, the entropy, the heat capacity, etc., as functions of the masses only when the pressure and temperature of the system are constant, and, consequently, the same general method of partial differentiation may be applied. In general, if we let G equal the value of the property of 1 mol of the whole phase, we have the following three fundamental and useful equations of partial molal quantities, namely,

$$\partial G = \overline{G}_1\partial N_1 + \overline{G}_2\partial N_2 + \cdots + \overline{G}_c\partial N_c, \tag{31}$$

$$G = \overline{G}_1 N_1 + \overline{G}_2 N_2 + \cdots + \overline{G}_c N_c, \tag{32}$$

$$o = N_1\partial\overline{G}_1 + N_2\partial\overline{G}_2 + \cdots + N_c\partial\overline{G}_c. \tag{33}$$

By the use of the general thermodynamic equations of Gibbs and the consideration of units, we are thus brought into contact with a class of quantities which are of utmost importance in the thermodynamics of solutions. The development of this subject since the time of Gibbs, and, particularly, the methods of employing the partial molal quantities in numerical calculations have been brought about very largely by the researches of Lewis and his colleagues.[1] In the present discussion, some of their methods will be employed as the occasion may arise, but no attempt will be made to give a comprehensive treatment of the subject.

The Direct Determination of Partial Molal Heat Content from Calorimetric Data: The physical significance of partial quantities may be clearly understood

[1] These investigations have been revised and corrected and a very comprehensive treatment of the subject has been presented by Lewis and Randall, Thermodynamics. McGraw-Hill Book Co. (1923).

by considering the heat of dilution by water of a salt solution of a given concentration. We may employ for this purpose the data of Stearn and Smith [1] on the heat of dilution of a 2.9 molal strontium chloride solution by different quantities of water. The results which are given in Table IV were carried out at 25° and 1 atmosphere. If the heat of dilution is positive, the system evolves heat as a result of the change, and, consequently, there will be a decrease in heat content or vice versa.

TABLE IV

HEAT CONTENT DECREASE, AND MOLAL HEAT CONTENT DECREASE OF A 2.9M STRONTIUM CHLORIDE ON DILUTION BY DIFFERENT QUANTITIES OF WATER

Δn_1	$(-\Delta H)$	$\frac{(-\Delta H)}{\Delta n_1}$
Water of Dilution (Mols.)	Total Heat of Dilution (Cals.)	Mean Heat Content Decrease per Mol. (Cals.)
37.2	129.8	3.49
30.0	112.4	3.75
30.0	114.1	3.80
27.7	109.2	3.95
20.0	86.3	4.31
19.5	85.4	4.38
10.0	48.5	4.85

In Fig. 1, the values of $\frac{(-\Delta H)}{\Delta n_1}$ are plotted against the number of mols of water added. This plot is a straight line and, consequently, the results may be extrapolated to zero Δn_1. It is thus found that $\frac{(-\Delta H)}{\Delta n_1}$ equals 5.4 when Δn_1 equals zero. This is exactly the definition of the derivative of H with respect to n_1, and, since it refers to the heat content change produced by one of the components while the mass of the other component is constant, it equals the negative of $\frac{\partial H}{\partial n_1}$, or $\bar{H}_1$, the partial molal heat content of the component water. Or, we may equally well say that $\bar{H}_1$ equals the change of heat content of an infinitely large quantity of the solution on the addition of a mol of water.

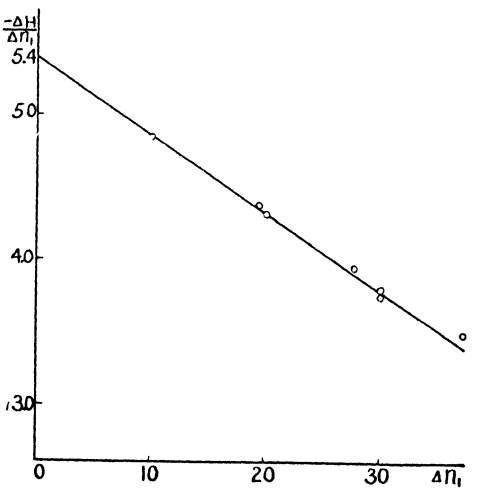


FIG. 1. Molal Heat Content Decrease of Strontium Chloride

[1] *J. Am. Chem. Soc.*, **42**, 18 (1920).

By a series of measurements of this kind, Stearn and Smith have obtained the partial molal heat content of water in strontium chloride solutions of different concentrations. In tabulating a partial molal quantity, it is necessary to refer its value to another standard state. It is convenient to employ as a standard state an infinitely dilute solution of an electrolyte. Thus, for a change in a partial molal quantity of the water or strontium chloride in the above solution, we would have $(\overline{G}_1 - \overline{G}_1^0)$ and $(\overline{G}_2 - \overline{G}_2^0)$, respectively. In all the subsequent discussion the subscript 1 will refer to the water, and the subscript 2 to the electrolyte. The partial molal quantity of the solvent in pure solvent, or $\overline{G}_1^0$, is zero and, consequently, this case is very simple. Following throughout the notation of Lewis and Randall, we shall let these differences of partial heat contents equal $\overline{L}_1$, $\overline{L}_2$, respectively, and call these quantities the relative partial molal heat contents. In Table V, the data of Stearn and Smith on the relative partial heat contents of water at different molal concentrations of strontium chloride are given.

TABLE V

RELATIVE PARTIAL MOLAL HEAT CONTENTS OF WATER IN STRONTIUM CHLORIDE SOLUTIONS AT 25°

c	$\overline{L}_1$
0	0.00
0.20	− 0.25
0.425	− 0.50
0.80	− 0.62
1.20	− 0.90
1.55	− 1.11
2.00	− 1.75
2.4	− 2.10
2.9	− 5.40
3.2	− 7.20

Relative Partial Molal Heat Content of Hydrochloric Acid from Electromotive Force Data: In an earlier section, it was shown that, from electromotive force measurements, it was possible to obtain the free energy change accompanying the transfer of a mol of hydrochloric acid from a solution of one concentration to a solution of another concentration. It was also shown that this change could be regarded as the difference of two quantities, which are the free energy changes on adding a mol to very large quantities of the solutions, respectively. It is clear now that these quantities are really the partial derivatives of the free energies with respect to the number of mols of the component in question, and that the electromotive force method measures the partial molal free energy change of the component transferred by the cell reaction. Further, by measuring the temperature coefficients of these cells, it was also found possible to compute the differences in partial molal heat contents of the electrolyte transferred. We shall now confine our attention more closely to the properties of these quantities, and consider the partial molal heat

content and free energy of hydrochloric acid obtained from the data of Ellis [1] and Noyes and Ellis.[2]

In Table VI, their data on the decreases in heat content of transfer in joules at 25° of a mol of hydrochloric acid from a solution of concentration c to a concentration 0.1 molal have been compiled.

TABLE VI

DECREASE IN HEAT CONTENT AND FREE ENERGY WHEN 1 MOL OF HYDROCHLORIC ACID IS TRANSFERRED FROM c TO 0.100M AT 25°

c	$(-\Delta\overline{H})$	$(-\Delta\overline{F})$
4.484	8474	23544
1.928	3591	15744
1.038	1937	11679
0.771	1619	9971
0.509	999	7757
0.338	260	5856
0.1	0	0
0.0332	− 435	− 5138
0.00948	− 745	− 11044
0.00338	− 915	− 15898
0.000999	− 930	− 21878
0	− 1050 (extrapolated)	− ∞

It is important to note from these data that $(-\Delta\overline{F})$ approaches $-\infty$ as c approaches zero, and that this behavior is quite different from the variation of $(-\Delta\overline{H})$ with the concentration. We shall reserve the discussion of the partial molal free energy for a later section and devote our attention to the partial molal heat content change. In Fig. 2 have been plotted the values of $(-\Delta\overline{H})$ and $c^{1/2}$ at the lower concentrations. This curve is a straight line and, consequently, may be extrapolated to zero concentration. This extrapolated value is − 1050. Assigning in the customary way the value $\overline{H}_2^0$ for the partial heat content of the acid at zero concentration, the values of $\overline{L}_2$ or $(\overline{H}_2 - \overline{H}_2^0)$ at round concentrations have been read off a plot of the results in Table VI. These results have been converted to calories by dividing by 4.182 and are given in the fourth column of Table VII.

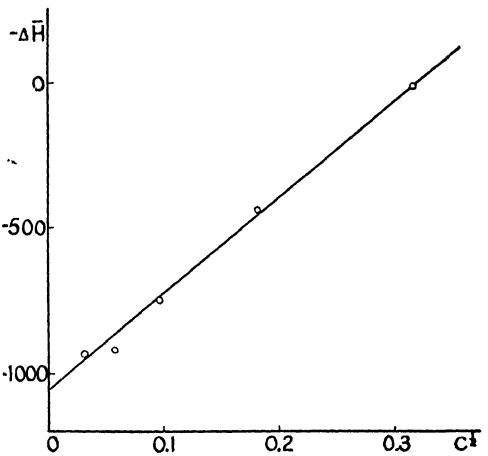


FIG. 2. Molal Heat Content Decrease of Hydrochloric Acid

The Calculation of a Relative Partial Molal Heat Content of Water from the Relative Partial Heat Content of Hydrochloric Acid: According to

[1] Ellis, *J. Am. Chem. Soc.*, **38**, 737 (1916).

[2] *J. Am. Chem. Soc.*, **39**, 2532 (1917). The cells employed by these investigators have been considered in an earlier section.

equation (32),

$$H = N_1\bar{H}_1 + N_2\bar{H}_2 \tag{34}$$

and

$$H_0 = N_1\bar{H}_1^0 + N_2\bar{H}_2^0, \tag{35}$$

whence L, the total relative heat content, $(H - H_0)$, will be

$$L = N_1\bar{L}_1 + N_2\bar{L}_2. \tag{36}$$

Further, according to (33),

$$0 = N_1\partial\bar{L}_1 + N_2\partial\bar{L}_2. \tag{37}$$

By means of this latter equation, it is possible to determine the value of the relative partial molal heat content of one component when that of the other component is known. For example, by rearranging and integrating (37), the relative partial molal heat content, $\bar{L}_1$, of the water in the hydrochloric acid solutions will be given by

$$\bar{L}_1 = -\int \frac{N_2}{N_1}\partial\bar{L}_2. \tag{38}$$

$\bar{L}_1$ will equal the negative of the integral of the right-hand member, which expression may be easily evaluated by a graphical method. Fig. 3 contains a plot of $\frac{N_2}{N_1}$ against $\bar{L}_2$, the relative partial molal heat content of the acid. At a given concentration, or value of $\frac{N_2}{N_1}$, the area under this curve from 0 to $\frac{N_2}{N_1}$ equals this integral, and also the negative of $\bar{L}_1$. This area was easily evaluated from the plot by counting squares. The results obtained are compiled at round concentrations in the third column of Table VII. In the fifth and sixth columns of this table, for the sake of comparison, are also included $\bar{L}_1$, the relative partial molal heat content of water in aqueous sodium chloride solutions, and $\bar{L}_2$, the relative partial molal heat content of sodium chloride in the same solutions. These were obtained at the designated concentrations from a curve of the results of Lewis and Randall.[1]

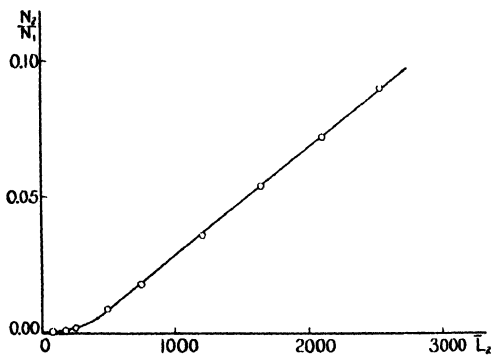


FIG. 3. Relative Partial Molal Heat Content of Hydrochloric Acid

[1] Thermodynamics, Chapter VIII, Table 5. The experimental data employed were obtained by Randall and Bisson, *J. Am. Chem. Soc.*, **42**, 347 (1920).

TABLE VII

RELATIVE PARTIAL MOLAL HEAT CONTENTS (IN CALORIES) OF HYDROCHLORIC ACID AND WATER IN HYDROCHLORIC ACID SOLUTIONS AND SODIUM CHLORIDE AND WATER IN SODIUM CHLORIDE SOLUTIONS

c	$\frac{N_2}{N_1}$	HCl		NaCl	
		$\bar{L}_1$	$\bar{L}_2$	$\bar{L}_1$	$\bar{L}_2$
0	0	0	0	0	0
0.001	0.000018	—	25.1	—	—
0.01	0.00018	− 0.012	78.9	0.01	− 1
0.05	0.0009	− 0.052	177	0.03	− 3
0.1	0.0018	− 0.161	251	0.05	− 8
0.5	0.009	− 1.16	496	0.65	− 120
1	0.018	− 3.66	747	3.4	− 332
2	0.036	− 15.8	1206	10.0	− 564
3	0.054	− 37.7	1651	17.4	− 736
4	0.072	− 66.6	2103	21.9	− 810
5	0.09	− 103.6	2541	19.4	− 779

It is important to note that $\bar{L}_1$ is negative in hydrochloric acid solutions and positive in sodium chloride solutions, and that $\bar{L}_2$ is positive in hydrochloric acid solutions and negative in sodium chloride solutions.

Partial Molal Heat Content and Free Energy of Hydrochloric Acid in Acid-Salt Mixtures: By measuring the electromotive forces of cells of the types

$$H_2\ (1\ atm.)\,|\,HCl\ (0.1M)\,|\,HgCl\,|\,Hg$$

and

$$H_2\ (1\ atm.)\,|\,HCl\ (0.1M) + MeCl_x\ (c)\,|\,HgCl\,|\,Hg$$

and their temperature coefficients, it is possible to compute the partial free energy and heat content of hydrochloric acid in the salt solutions. The cell reaction of the first cell is

$$\tfrac{1}{2}H_2\ (1\ atm.) + HgCl = Hg + HCl\ (0.1M)$$

and the second cell is

$$\tfrac{1}{2}H_2\ (1\ atm.) + HgCl = Hg + HCl\ (0.1M)\ [MeCl_x\ (c)],$$

since the hydrochloric acid is produced in a solution of 0.1M hydrochloric acid containing the chloride at a concentration c. By subtracting the second equation from the first, we obtain

$$HCl\ (0.1M)\ [MeCl_x\ (c)] = HCl\ (0.1M),$$

which represents the transfer of a mol of hydrochloric acid from the mixture to a 0.1M hydrochloric acid solution. Thus, the free energy and heat content decreases of transfer of the acid, or the changes in partial molal free energy and heat content, may be computed from measurements of the free energy and heat

content decreases of the cell reaction. In Table VIII are given the relative partial free energies ($\overline{F}_2 - \overline{F}_{2(0.1)}$) and heat contents ($\overline{H}_2 - \overline{H}_{2(0.1)}$) of the hydrochloric acid in solutions of potassium, sodium and lithium chlorides referred to 0.1M hydrochloric acid, computed from the data of Harned.[1]

TABLE VIII

RELATIVE PARTIAL FREE ENERGY AND HEAT CONTENT OF HYDROCHLORIC ACID IN UNIUNIVALENT SALT SOLUTIONS

	c	$(\overline{F}_2 - \overline{F}_{2(0.1)})$ (joules)	$(\overline{H}_2 - \overline{H}_{2(0.1)})$	
			(joules)	(cals.)
(1) KCl	0.202	2387	3	0.72
	0.509	4016	18	4.3
	1.035	5662	75	17.9
	2.134	7987	685	164.0
	3.309	9898	1403	336.0
(2) NaCl	0.201	2430	71	17.0
	0.506	4160	136	32.5
	0.918	5649	284	68
	1.023	5965	377	90
	1.871	8083	1186	284
	2.094	8566	1190	285
	2.711	9844	1797	430
	3.202	10817	2323	555
	3.726	11762	2971	710
(3) LiCl.....	0.420	3890	—	—
	0 848	5778	703	168
	1.727	8397	2064	486
	2.636	10714	3263	780
	3.574	12944	4600	1100
	4.556	15192	5805	1390

The Partial Molal Free Energy and Concentration of an Electrolyte: In the above discussion, it was found that the partial molal heat contents of both the water and the electrolyte in the two component solutions approached a limiting value as the concentration approached zero. The behavior of the partial free energy is quite different. To illustrate this, we plot in Fig. 4 the typical values of $(-\Delta\overline{F})_{298}$ of a uniunivalent electrolyte obtained from Table VI against the logarithm of the concentration. The resulting curve approaches a straight line as c decreases. The limiting value of the slope of this curve as c approaches 0 is 2×5708.1 joules. If the natural logarithm of the concentration had been plotted, this slope would be equal to 2×2479.0 joules, which in turn is equal to $2 \times RT$, where R is the gas constant in joules, and T is the absolute temperature, or 298.1. Thus, as a law, only to be regarded as exactly

[1] *J. Am. Chem. Soc.*, **42**, 1808 (1920).

valid in infinitely dilute solution, for the relative partial free energy of a uni-univalent electrolyte at constant temperature, we have

$$\overline{F} - \overline{F}_0 = 2RT\ln c + I, \tag{39}$$

where I is a constant and is a function of an arbitrary standard state, $\overline{F}_0$. This equation will be equally valid for any uniunivalent electrolyte, and at any temperature, providing the partial free energy differences are measured at constant temperature. Similarly for a biunivalent or a triunivalent salt in very dilute solutions, we obtain

$$\overline{F} - \overline{F}_0 = 3RT\ln c + I$$

and

$$\overline{F} - \overline{F}_0 = 4RT\ln c + I, \tag{39a}$$

respectively. Since electrolytes approach complete dissociation as their concentration approaches zero, the range of validity of these equations would probably be extended if the true ion concentration were employed, instead of the molal concentration, c. Upon differentiation, we would obtain for any electrolyte

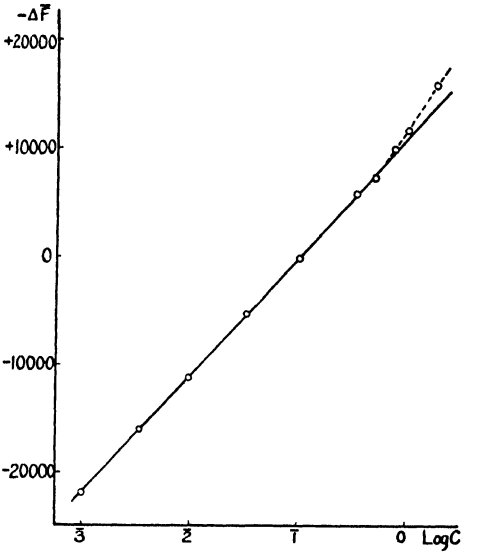


FIG. 4. Molal Free Energy of Hydrochloric Acid

$$\partial\overline{F} = \nu RT\partial\ln c_{\pm}, \tag{40}$$

where ν is the sum of the number of anions and cations formed by dissociation and $c_{\pm}$ is the true degree of dissociation times c. For a change in partial free energy in very dilute solutions between two concentrations, it is obvious that

$$\overline{F}_2 - \overline{F}_1 = \nu RT\ln\frac{c_{\pm}''}{c_{\pm}'}. \tag{41}$$

The partial free energy is greater in the solution of higher concentration, and thus a transfer from a higher to a lower concentration, or from $c_{\pm}''$ to $c_{\pm}'$, is accompanied by a decrease in free energy. It will be shown in the subsequent discussion that (40) and (41) are particular expressions of a more general limiting law which includes gases, undissociated solutes and ions.

As a result of these considerations, it follows that the partial molal free energy becomes $-\infty$ at zero concentration, and, for this reason, special methods, not required in calculating partial molal heat contents, are necessary in calculating the partial free energies. We are thus led to the consideration

of another thermodynamic function which will be shown to be very useful in subsequent calculations.

The Activity Function

In two papers, G. N. Lewis [1] introduced two new functions, the fugacity and the activity, into thermodynamic chemistry. In these papers these functions were defined, nearly all of their important relations with the other thermodynamic functions and the variables of condition were deduced, and their usefulness predicted. Since the first of these papers, and, particularly, since 1912, a large literature on this subject has developed, which is devoted, principally, to studies of the activities of electrolytes and ions in aqueous solutions. A most comprehensive calculation and discussion of this recent work has been made by Lewis and Randall.[2]

In his first papers, Lewis developed the thermodynamics of the fugacity and activity functions from some fundamental definitions, and the laws of thermodynamics, by a cyclic method. This laborious method has now been abandoned, and a mathematically simpler development, using the thermodynamic functions, has been adopted. We shall employ the latter, for, aside from its simplicity, it conforms well with the recent methods of treatment of Bronsted,[3] Bjerrum [4] and others. Since the activity has been used exclusively in the study of solutions of electrolytes, we shall simplify the present treatment of the subject by omitting any consideration of the fugacity.[5]

Before proceeding to the discussion, it should be understood that these useful functions have been introduced in order to simplify and render exact many complicated thermodynamic calculations. Their introduction adds nothing new to the content of thermodynamic theory, and they are not so important as the more fundamental functions such as the entropy and free energy.

Definition of Activity: A convenient method of defining the activity of a component of a system is by the equation

$$F = RT\ln\xi + i, \tag{42}$$

where ξ is the activity in general and i is a constant.

The free energy has no absolute value and, consequently, is measured in reference to some standard state, F_0. Thus

$$F - F_0 = RT\ln\frac{\xi}{\xi_0} = RT\ln a, \tag{43}$$

where ξ_0 is the activity when $(F - F_0)$ is equal to zero. $\frac{\xi}{\xi_0}$ is then the relative activity (a), and it is in this sense that the function is commonly employed.

Similarly, the relative activity of a molecular or ionic species in a phase of

[1] *Proc. Am. Acad.*, **37**, 45 (1901); **43**, 259 (1907).

[2] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921); Thermodynamics, Chaps. XXII to XXVII inclusive.

[3] *J. Am. Chem. Soc.*, **42**, 761 (1920).

[4] *Z. physik. Chem.*, **104**, 406 (1923).

[5] Lewis and Randall, Thermodynamics, Chaps. XVII–XX inclusive.

variable composition will be related to the partial free energy by the equation

$$\overline{F} - \overline{F}_0 = RTlna. \tag{44}$$

The relative activity will be called the activity in all subsequent discussions.

The Equilibrium Constant of a Chemical Reaction: Let us now consider a reaction at constant temperature and pressure in which n_1 mols of A_1, etc., n_2 mols of A_2, etc., and n_3 mols of A_3, etc., react to form n_1' mols of A_1', etc., n_2' mols of A_2', etc., and n_3' mols of A_3', etc., where the mols with the subscript 1 refer to gases, 2 to solutions, and 3 to liquids and solids. Thus

$$n_1A_1 + \cdots n_2A_2 + \cdots n_3A_3 + \cdots = n_1'A_1' + \cdots n_2'A_2' + \cdots n_3'A_3'.$$

According to equations (43) and (44),

$$(F - F_0)_{A_1} = n_1RTlna_{A_1}, \text{ etc.},$$
$$(\overline{F} - \overline{F}_0)_{A_2} = n_2RTlna_{A_2}, \text{ etc.},$$

and

$$(F - F_0)_{A_1'} = n_1'RTlna_{A_1'}, \text{ etc.},$$
$$(\overline{F} - \overline{F}_0)_{A_2'} = n_2'RTlna_{A_2'}, \text{ etc.}$$

The total change in free energy of the reaction will be

$$[(F - F_0)_{A_1'} + (\overline{F} - \overline{F}_0)_{A_2'} + \cdots] - [(F - F_0)_{A_1} + (\overline{F} - \overline{F}_0)_{A_2} + \cdots]$$
$$= RTln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots}.$$

If we let

$$\Delta F = (F_{A_1'} + \overline{F}_{A_2'} + \cdots) - (F_{A_1} + \overline{F}_{A_2} + \cdots)$$

and

$$\Delta F_0 = (F_{0A_1'} + \overline{F}_{0A_2'} + \cdots) - (F_{0A_1} + \overline{F}_{0A_2} + \cdots),$$

we obtain

$$\Delta F - \Delta F_0 = RTln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'}}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3}}. \tag{45}$$

ΔF is the free energy change of the reaction in general, and $(\Delta F - \Delta F_0)$ is the free energy change of the reaction in reference to the standard state.

When the reaction is in equilibrium at constant temperature and pressure, the condition that

$$\Delta F = 0 \tag{21}$$

must be fulfilled, and, consequently,

$$\Delta F_0 = -RTln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots}. \tag{46}$$

Since ΔF_0 is a constant, we have at constant temperature

$$K = \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots}, \tag{47}$$

where K is the equilibrium constant of the reaction. This general equation, which is entirely similar in form to the mass action law, has the advantage of being exact.

The Activity Product, the Mean Activity Product, and the Activity Coefficient of an Electrolyte: The equilibrium constant of dissociation of a uni-univalent electrolyte may now be written

$$K = \frac{a_+ a_-}{a_2}, \tag{48}$$

where a_+, a_- are the activities of the cation and anion, respectively, and a_2 is the activity of the undissociated molecule. According to equation (46),

$$\Delta F_0 = -RT\ln\frac{a_+'' a_-''}{a_2''} = RT\ln a_2'' - RT\ln a_+'' a_-''$$

and

$$\Delta F_0 = -RT\ln\frac{a_+' a_-'}{a_2'} = RT\ln a_2' - RT\ln a_+' a_-',$$

where the primes and double primes refer to solutions of two different concentrations, respectively. Since ΔF_0 is constant, by subtracting the second of these equations from the first, and letting $\overline{F}_1$ and $\overline{F}_2$ be the partial free energies at the two concentrations, respectively, we obtain according to equation (44)

$$\overline{F}_2 - \overline{F}_1 = RT\ln\frac{a_2''}{a_2'} = RT\ln\frac{a_+'' a_-''}{a_+' a_-'}. \tag{49}$$

In view of the fact that in solutions of strong electrolytes the concentration of the undissociated molecule is unknown, and since our chief concern is with partial molal free energy differences and activity ratios, we let the equilibrium constant equal 1, and define the activity of the electrolyte by

$$a_2 = a_+ a_-$$

and the mean activity of the electrolyte by

$$a_\pm = (a_+ a_-)^{1/2}.$$

Further, the activity coefficient of a uniunivalent electrolyte is defined as the mean activity product of its ions divided by the molal concentration of the electrolyte. The activity coefficient, γ, of a uniunivalent electrolyte will be accordingly

$$\gamma = \frac{a_\pm}{c} = \left(\frac{a_+ a_-}{c^2}\right)^{1/2} \tag{50}$$

or the square root of the product of the activity coefficients of the ions. In general, if we consider the dissociation of any strong electrolyte of a molal concentration c according to

$$C_{\nu^+}A_{\nu^-} \doteq \nu^+ C^+ + \nu^- A^-,$$

we shall have

$$a_2 = a_+^{\nu^+} a_-^{\nu^-}$$

and

$$a_\pm = (a_+^{\nu^+} a_-^{\nu^-})^{1/\nu},$$

where ν, the total number of ions formed, will equal $\nu^+ + \nu^-$. The activity coefficient will be given by

$$\gamma = \left(\frac{a_+^{\nu^+} a_-^{\nu^-}}{(\nu^+ c)^{\nu^+} (\nu^- c)^{\nu^-}} \right)^{1/\nu} = \frac{a_\pm}{c(\nu^{+\nu^+} \nu^{-\nu^-})^{1/\nu}} \tag{51}$$

or the νth root of the product of the activity coefficients of the ions.

The Free Energy Increment of a Perfect Gas and Perfect Solute at Constant Temperature: According to equation (6), the free energy is

$$F = A + pv, \tag{6}$$

which upon differentiation becomes

$$dF = dA + pdv + vdp.$$

In any reversible isothermal expansion or compression of a gas, the decrease in A will equal the maximum work, or

$$dA = -pdv,$$

and, therefore,

$$\partial F = vdp.$$

Since, for a perfect gas, $pv = RT$, we obtain

$$\partial F = RT\partial lnp = RT\partial lnc. \tag{52}$$

For a finite change between two concentrations, it is evident that

$$F_2 - F_1 = RTln\frac{c_2}{c_1}. \tag{53}$$

If the process consists of an expansion, or $c_1 > c_2$, it will be accompanied by a decrease in free energy.

In an analogous manner, on the assumption of the validity of van't Hoff's law ($\pi = cRT$) for perfect solutes, it can be shown that

$$\partial \overline{F} = RT\partial lnc, \tag{54}$$

where $\overline{F}$ and c are the partial free energy and concentration of the solute.

Equations (52) and (54), which are exactly analogous to equation (40), approach exact validity as c approaches zero.

The Limiting Law for Dilute Molecular and Ionic Species: From the fundamental definition of the activities of gases, undissociated solutes and

electrolytes, we obtain by differentiation the equations at constant temperature

$$\partial F = RT\partial \ln a, \tag{55}$$

$$\partial \overline{F} = RT\partial \ln a, \tag{56}$$

$$\partial \overline{F} = \nu RT\partial \ln a_{\pm}, \tag{57}$$

respectively. We may now state the limiting law for molecular and ionic species at high dilutions in the following simple manner: *The activities of all molecules and ions approach proportionality to their concentrations as their concentrations approach zero.* It is at once obvious that equations (55), (56) and (57) become equal to (52), (54) and (40) as the concentrations of the species under consideration approach zero. (40), (52) and (54) are, consequently, particular cases of a general law. From this law and the definition of the activity, the law for ideal gases, van't Hoff's law for undissociated molecules, and Raoult's law may be deduced.[1] As a result of this important property of the activity of ions and molecules, the general expression for the equilibrium constant of a reaction (equation 47) approaches in value the well-known mass action law

$$K = \frac{c_{A_1'}^{n_1'} \cdots c_{A_2'}^{n_2'} \cdots}{c_{A_1}^{n_1} \cdots c_{A_2}^{n_2} \cdots}, \tag{56}$$

as the concentrations of the gas and solute components approach zero. The law of mass action is thus shown to be a limiting law, which will not be valid in gas systems at high pressures, and solutions of high concentrations.

Attempts to apply the law of mass action to solutions of strong electrolytes in aqueous solutions have always met with failure with the possible exception of some results obtained with very dilute solutions. This is due both to an inadequate knowledge of the true concentrations of the ions and molecules in the solution, and to the fact that the classic mass action law has been employed. The general law of mass action expressed by equation (47) should prove of great value in the future for calculating the inner equilibrium of solutions.

Activity and Temperature: We have found that the variation of the free energy with the temperature is given by

$$\frac{\partial\left(\frac{F}{T}\right)}{\partial T} = -\frac{H}{T^2}, \tag{17}$$

where F and H are to be referred to arbitrary standard states. Further, according to equation (29), the free energy of a phase of c components is expressed by

$$F = N_1\overline{F}_1 + N_2\overline{F}_2 + \cdots + N_c\overline{F}_c, \tag{29}$$

[1] The ideal gas laws are immediately deducible. From (55) and the limiting law, $v\partial p = RT\partial \ln c$, or $\partial p = RT\partial c$, whence by integration $pv = RT$ since the integration constant is zero.

or, if each of these quantities be referred to arbitrary standard states,

$$F - F^0 = N_1(\overline{F}_1 - \overline{F}_1^0) + N_2(\overline{F}_2 - \overline{F}_2^0) + \cdots + N_c(\overline{F}_c - \overline{F}_c^0) \quad (58)$$

is obtained. We may now introduce the activities by equation (44) and obtain

$$F - F^0 = N_1 RT ln a_1 + N_2 RT ln a_2 + \cdots + N_c RT ln a_c. \quad (59)$$

Similarly, according to the general equation for partial quantities and equation (36), the total heat content will be

$$H - H^0 = N_1\overline{L}_1 + N_2\overline{L}_2 + \cdots + N_c\overline{L}_c. \quad (60)$$

Substituting these values of $(F - F^0)$ and $(H - H^0)$ for F and H in equation (17), and performing the differentiation at constant composition, we obtain

$$\left[\frac{N_1 \partial ln a_1 + N_2 \partial ln a_2 + \cdots + N_c \partial ln a_c}{dT}\right]_{p,\,N} = \frac{-(N_1\overline{L}_1 + N_2\overline{L}_2 + \cdots N_c\overline{L}_c)}{RT^2}. \quad (61)$$

This is the general equation for the variation of the activities of the components of a mixture with the temperature and at constant composition.

Let us consider the case where "1 mol of solution," which consists of N_1 mols of the first component, N_2 mols of the second component, etc., is transferred from a solution of one composition to that of another composition. In this case, the partial free energy and heat content increments will be

$$F'' - F' = N_1(\overline{F}_1'' - \overline{F}_1') + N_2(\overline{F}_2'' - \overline{F}_2') + \cdots + N_c(\overline{F}_c'' - \overline{F}_c') \quad (58a)$$

$$= N_1 RT ln \frac{a_1''}{a_1'} + N_2 RT ln \frac{a_2''}{a_2'} + \cdots + N_c RT ln \frac{a_c''}{a_c'} \quad (59a)$$

and

$$H'' - H' = N_1(\overline{L}_1'' - \overline{L}_1') + N_2(\overline{L}_2'' - \overline{L}_2') + \cdots + N_c(\overline{L}_c'' - \overline{L}_c'). \quad (60a)$$

Substituting these values for ΔF and ΔH in equation (18), and performing the differentiation at constant composition,

$$\left[\frac{N_1 \partial ln \frac{a_1''}{a_1'} + N_2 \partial ln \frac{a_2''}{a_2'} + \cdots + N_c \partial ln \frac{a_c''}{a_c'}}{\partial T}\right]_{p,\,N} = -\frac{[N_1(\overline{L}_1'' - \overline{L}_1') + N_2(\overline{L}_2'' - \overline{L}_2') + \cdots N_c(\overline{L}_c'' - \overline{L}_c')]}{RT^2}. \quad (61a)$$

Usually, the transfer of 1 mol of a single component is considered. In this

case, it is obvious that

$$\frac{\partial\left(ln\frac{a''}{a'}\right)}{\partial T} = -\frac{(\overline{L}'' - \overline{L}')}{RT^2}. \tag{62}$$

Although many symbols are required to perform these deductions accurately, the principles involved are quite simple. If 1 mol of a component is transferred, then ΔF is the partial free energy change and ΔH is the relative partial heat content change of the transfer. If 1 mol of solution is transferred, then ΔF is the mol fraction times the partial free energy change of the first component plus the mol fraction times the partial free energy change of the second component, etc., and ΔH is the mol fraction times the relative partial heat content change of the first component plus, etc.

In order to integrate equation (62), or others like it, it is necessary to know $(\overline{L}'' - \overline{L}')$ as a function of the temperature. Such a relation is given by equation (11), from which it is clear that

$$\frac{\partial(\overline{L}'' - \overline{L}')}{\partial T} = \overline{C}_p'' - \overline{C}_p', \tag{63}$$

where $\overline{C}_p''$ and $\overline{C}_p'$ are the partial molal specific heats at constant pressure at the two concentrations, respectively.

Activity and Pressure: We have already found for the differential of the free energy at constant composition

$$\partial F = -S\partial T + v\partial p, \tag{13}$$

whence by differentiation with respect to p, at constant temperature, we obtain

$$\left[\frac{\partial F}{\partial p}\right]_T = v. \tag{64}$$

According to the general equation for partial quantities, the total volume V will be given by

$$V = N_1\overline{V}_1 + N_2\overline{V}_2 + \cdots + N_c\overline{V}_c, \tag{65}$$

where $\overline{V}_1$, $\overline{V}_2$, etc., are the partial volumes. Substituting for F the value given by (59), and for V the value given by (65), we obtain

$$\left[\frac{N_1\partial lna_1 + N_2\partial lna_2 + \cdots + N_c\partial lna_c}{\partial p}\right]_{T,\,N} = \frac{N_1\overline{V}_1 + N_2\overline{V}_2 + \cdots + N_c\overline{V}_c}{RT} \tag{66}$$

and for a single component

$$\left[\frac{\partial lna}{\partial p}\right]_{T,\,N} = \frac{\overline{V}_1}{RT}. \tag{67}$$

The Condition of Equilibrium of a Polycomponent System in More than One Phase at Constant Pressure and Temperature: As previously mentioned, Gibbs proved the general case that when a c component system in P phases is in equilibrium at constant temperature and pressure, the values of the chemical potential, $\frac{\partial F}{\partial m}$, of each component will be the same in each phase (equation 25). That this is true for a particular case can be immediately seen by considering the distribution of a component between two liquid phases at constant temperature and pressure, and the process of transfer of the component from one phase to the other. Any change in free energy in such a process will equal the difference in partial free energies of the component in the two phases, respectively. But the criterion of equilibrium at constant temperature and pressure is that $\partial F = 0$, and, consequently, the partial free energies of the component in the two phases must be equal. This is equivalent to the statement that at equilibrium the activities of the component in the two phases are equal. If the partial free energy of the component is greater in the first phase than in the second, we have found that it will tend to pass from the first phase to the second with an accompanying loss in free energy. Consequently, when the activity of a component distributed through two phases is greater in the first phase than in the second, the component may pass from the first phase to the second.

Summary: In this section, the important properties of the activity function have been discussed and the general equations have been deduced. The properties of this function have been shown to rest on the definition of the relative activity, which for a component of a one-component system is

$$F - F_0 = RT\ln a, \tag{43}$$

and for a component in a phase of more than one component is

$$\overline{F} - \overline{F}_0 = RT\ln a. \tag{44}$$

The limiting law for molecular or ionic species at high dilutions has been stated as follows: "The activities of all molecules and ions approach proportionality to their concentrations as their concentrations approach zero." From this law and the definitions of activities, the gas laws and the laws of dilute solutions may be readily deduced.

It has been found that if the activity of a substance distributed through two phases is greater in the first phase than in the second, it may pass spontaneously from the first phase to the second. The criterion of stable equilibrium is that the activities of all components distributed through all phases be equal.

By employing the activity function, a general law of equilibrium may be deduced, of which the law of mass action is a special case, valid in dilute systems, and exact in infinitely dilute systems.

The general equations which express the relations of the activities of a phase of more than one component to the variables, pressure, temperature and composition are:

(1) *Temperature and Pressure Constant:* From (30) and the definition of activity,

$$\left[\frac{N_1\partial\ln a_1 + N_2\partial\ln a_2 + \cdots + N_c\partial\ln a_c}{\partial N}\right]_{p,\,T} = 0. \tag{68}$$

(2) *Pressure and Composition Constant:*

$$\left[\frac{N_1\partial \ln a_1 + N_2\partial \ln a_2 + \cdots + N_c\partial \ln a_c}{\partial T}\right]_{p,N} = -\frac{[N_1\overline{L}_1 + N_2\overline{L}_2 + \cdots + N_c\overline{L}_c]}{RT^2}. \quad (61)$$

(3) *Temperature and Composition Constant:*

$$\left[\frac{N_1\partial \ln a_1 + N_2\partial \ln a_2 + \cdots + N_c\partial \ln a_c}{\partial p}\right]_{T,N} = \frac{N_1\overline{V}_1 + N_2\overline{V}_2 + \cdots + N_c\overline{V}_c}{RT}.^{1} \quad (66)$$

Calculations of the Activity Coefficients of Strong Electrolytes

It is possible to determine the activity coefficient of an electrolyte by electromotive force measurements of cells without liquid junction, and from the measurements of any of the colligative properties of solutions. On closer examination, however, this is a task accompanied with considerable difficulty. The activity coefficient has been so defined that it must equal unity at zero concentration, and it is on this value that all other values must be based. As a consequence, it is necessary to extrapolate the experimental results to infinite dilution by graphical methods, or employ some empirical equation which expresses the colligative property as a function of the concentration, and then perform an integration between a finite and zero concentration. It is just such an extrapolation or calculation which is subject to considerable error, because of the difficulty in obtaining reliable or accurate measurements at very low concentrations.

Measurements of rise in boiling point involve too many experimental difficulties to furnish the desired degree of accuracy, and would give only the activity coefficients at the boiling point of the solution. The difficult measurement of the osmotic pressure would obviously not suffice.

In order to perform the graphical extrapolation without considerable error, it is necessary to have consistent and reliable data in the concentration range from 0.001 or less to 0.1 molal. According to the data of Lovelace, Frazer, and Sease,[2] a 0.0498 molal potassium chloride solution has a vapor pressure only 0.0293 mm. lower than the vapor pressure of water at 20°. Although vapor pressure measurements will be shown to be of great value at high concentrations, it is clear from the order of their magnitude that they would become increasingly less valuable as the concentration decreases.

The measurement of the lowering of the freezing point, which has been greatly improved in recent years by the newer methods of measuring temperature and temperature differences, is much more promising. But, in this case, the results of the measurement must be reliable

[1] These equations were originally deduced by Lewis, *Proc. Amer. Acad.*, **43**, 259 (1907). These considerations and equations will serve as a general basis for the thermodynamics of solutions, and may by simple transformations be adapted to a specific problem. In the following discussion, we shall apply this method to electromotive forces, freezing points, vapor pressures, solubilities, etc., of strong electrolytes, and compute by typical methods the values of the activities of these electrolytes.

[2] *J. Am. Chem. Soc.*, **43**, 102 (1921).

to within 0.0001°, or even less, to warrant an accuracy of 1 per cent in the calculated activity coefficients.

Theoretically, the electromotive force method should be the most accurate for, according to equation (41), the electromotive force of a concentration cell is roughly proportional to the logarithm of the ratio of the concentrations of the solutions in the two parts of the cell. With the galvanometers at present available, there should be little difference in accuracy in measuring a cell containing, in the first place, solutions of 1 and 0.1 molal concentrations, and, in the second place, solutions of 0.001 and 0.0001 molal concentrations. Consequently, the measurement of a reversible cell should yield equally accurate results in dilute and in concentrated solutions. The electromotive forces of many cells have been found to be reproducible to within a few hundredths of a millivolt in very dilute solutions, but it is probable that, in most cases, these measurements are not of great value for computing activity coefficients by extrapolation because of slight electromotive forces produced by side reactions, or other obscure causes depending on the methods of preparation and nature of the surfaces of the solids involved. These disturbing factors, which are negligible in concentrated solutions, are a great drawback to the electromotive force method of computing activity coefficients in very dilute solutions. It is very difficult indeed to discover whether such complications exist; still more difficult to discover why they exist, and to eliminate them. There are, however, some few cell measurements which are thought to be sufficiently exact at all concentrations down to 0.001 molal to warrant an extrapolation to zero concentration.

As a result of this cursory review of the available methods, it is clear that only by considerable experimental exactitude, as well as laborious calculation, and by comparison of results by different methods can certainty regarding the values for the activity coefficients be assured.

In Table IX, the activity coefficients of potassium chloride calculated from different data and computed by different investigators have been compiled. In column (1) is the molal salt concentration, column (2) the activity coefficient of potassium chloride at these concentrations, calculated by Lewis and Linhart,[1] and Lewis and Randall,[2] from the freezing point data of Adams [3] and the electromotive force data of MacInnes and Parker,[4] and Noyes and MacInnes.[5] Column (3) contains the activity coefficients of potassium chloride in dilute solutions calculated from the freezing point data of Flügel [6] which are as consistent as the data of Adams. Under column (4) are placed the values obtained by Noyes and MacInnes from electromotive force data. Column (5) contains values obtained by Harned [7] from freezing point, electromotive force and vapor pressure data.

These values differ by a few per cent even in the very dilute solutions. The values in columns (2) and (3) were both obtained from measurements of freezing point lowerings. The results of Adams in column (2), although no more consistent in themselves than Flügel's, are probably more reliable. The values in column (4) obtained from very reproducible electromotive force measurements not only do not agree with the values calculated from the freezing point data, but the activity coefficient-concentration function of these

[1] *J. Am. Chem. Soc.*, **41**, 1951 (1919).
[2] *J. Am. Chem. Soc.*, **43**, 1112 (1921).
[3] *J. Am. Chem. Soc.*, **37**, 494 (1915).
[4] *J. Am. Chem. Soc.*, **37**, 1445 (1915).
[5] *J. Am. Chem. Soc.*, **42**, 239 (1920).
[6] *Z. physik. Chem.*, **79**, 585 (1912).
[7] *J. Am. Chem. Soc.*, **44**, 252 (1922).

TABLE IX

ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE OBTAINED BY DIFFERENT INVESTIGATORS

(1)	(2)	(3)	(4)	(5)
0	1.000	1.000	1.000	1.000
0.0001	0.993	0.974	—	0.982
0.0005	0.984	0.954	—	0.970
0.001	0.977	0.942	0.979	0.961
0.005	0.946	0.904	0.923	0.926
0.01	0.922	0.879	0.890	0.903
0.05	0.840	—	0.790	0.821
0.1	0.794	—	0.754	0.779
0.5	0.682	—	0.638	0.652
1	0.634	—	0.593	0.600

values has not the same form as a similar function of the values in column (2). This will suffice for the present to illustrate the nature and magnitude of the difficulties which are encountered.

A more systematic resumé of the methods of calculating activity coefficients will be undertaken in the following sections.

Calculation by Extrapolation from Electromotive Force Data: We have seen that equation (49) is

$$\bar{F}_2 - \bar{F}_1 = RTln\frac{a_+''a_-''}{a_+'a_-'} = 2RTln\frac{a_\pm''}{a_\pm'} \qquad (49)$$

and $\bar{F}_2 - \bar{F}_1$ equals $(-\mathbf{NEF})$ of a concentration cell without liquid junction containing a uniunivalent electrolyte if the cell reaction transfer is from left to right according to C^+A^- (dil.) = C^+A^- (conc.). Therefore, if we let **E** represent the electromotive force of such a cell, and $\mathbf{E}_0$ the electromotive force of a standard state such that $a_\pm^0$ equals unity, we obtain, at 25°,

$$-(\mathbf{E} - \mathbf{E}_0) = \frac{2RT}{\mathbf{NF}} ln a_\pm = 0.1183 \log a_\pm. \qquad (69)$$

By subtracting $0.1183 \log c$ from both members, and remembering that γ equals $\frac{a_\pm}{c}$, we obtain

$$\mathbf{E}_0 - (\mathbf{E} + 0.1183 \log c) = 0.1183 \log \gamma. \qquad (70)$$

Since γ equals unity when c equals zero, the right-hand member of this equation vanishes, and $\mathbf{E}_0$ equals $(\mathbf{E} + 0.1183 \log c)$ at zero concentration. If sufficiently reliable results are available in dilute solutions, $\mathbf{E}_0$ may be evaluated graphically by extrapolating the plot of $(\mathbf{E} + 0.1183 \log c)$ against c, or, for the convenience of plotting, $c^{1/2}$. It is impossible to extrapolate directly partial molal free energy data, and, consequently, electromotive force data to infinite

dilution, since the partial free energy of an electrolyte equals $-\infty$ when c equals zero. By employing the activity coefficient, the extrapolation is made possible. This is one of the most important uses of the activity function.

Up to the present time, there appears to be available only the electromotive force measurements of one cell which are sufficiently accurate and reliable in very dilute solutions to permit the extrapolation with certainty. These are the measurements of Linhart [1] on the cell

$$H_2 | HCl\ (c) | AgCl | Ag.$$

By employing these values, and the above method of extrapolation, Linhart and later Lewis and Randall [2] obtained 0.2234 volt for $\mathbf{E}_0$. Substituting this value in equation (70), they computed the values of γ given in the sixth column of Table XII from the combined data of Linhart, Ellis [3] and Noyes and Ellis [4] on both the above cell and the cell

$$H_2 | HCl\ (c) | HgCl | Hg.$$ [5]

Although the electromotive force measurements are not usually sufficiently accurate in dilute solutions to be extrapolated, they have proved to be of great value for the calculation of activity coefficients in the more concentrated solutions. In the latter case, it is necessary to know the activity coefficient at a given concentration and then by equation (49) it may be calculated at another concentration. For this purpose, it has been customary for many investigators to assign to the activity coefficient the value of the conductance or conductance-viscosity ratio at some low concentration, and then base all subsequent calculations on this value. Although this method has proved useful for approximate calculation in the absence of other necessary data, its employment should not be regarded as exact because it is probable that the activity coefficient only equals the conductance ratio in infinitely dilute solutions. It is far better to base all calculations on measurements of electromotive force or freezing point data.

Activity Coefficients from Freezing Point Lowerings in Very Dilute Solutions: The first calculations of activity coefficients from freezing point data were made by Lewis.[6] Later the method has been developed in very dilute solutions by Lewis and Linhart,[7] and extended to concentrated solutions by Lewis and Randall.[8] These valuable studies indicate that this method is the most promising for securing activity coefficients of most electrolytes at very low concentrations. The exact but complicated calculation of the activity

[1] *J. Am. Chem. Soc.*, **39**, 2601 (1917); **41**, 1175 (1919).
[2] *J. Am. Chem. Soc.*, **43**, 1112 (1921).
[3] *J. Am. Chem. Soc.*, **38**, 737 (1916).
[4] *J. Am. Chem. Soc.*, **39**, 2532 (1917).
[5] First studied by Tolman and Ferguson. *J. Am. Chem. Soc.*, **34**, 232 (1912).
[6] *J. Am. Chem. Soc.*, **34**, 1631 (1912).
[7] *J. Am. Chem. Soc.*, **41**, 1951 (1919).
[8] *J. Am. Chem. Soc.*, **43**, 1112 (1921).

coefficient from freezing point lowerings at temperatures other than the freezing point of the solution (e.g., 25°) and at high concentrations has been made by Lewis and Randall in the cases of sodium chloride and sulphuric acid solutions. In the present discussion, a presentation of the calculation of Lewis and Linhart will be made, and the factors which must be included in order to extend the calculation to high concentrations will be indicated.

Consider the reaction

$$H_2O\ (l) = H_2O\ (s) + (-\Delta H).$$

$(-\Delta H)$ will equal the heat of fusion, or ΔH the heat of solidification. Let T_0 equal the temperature of the freezing point of pure water, T the temperature of the freezing point of the solution, and θ the lowering of the freezing point, and, therefore,

$$T = T_0 - \theta \qquad \text{and} \qquad dT = -d\theta.$$

In this case, the transfer is from the liquid to the solid. If, now, we let a' equal the activity of the liquid, and a'' the activity of the solid, we obtain the equation, similar to equation (62),

$$\frac{\partial ln \frac{a''}{a'}}{\partial T} = -\frac{\Delta H}{RT^2}. \tag{71}$$

If we choose as a reference state the condition that the activity of liquid water is unity at 0°, it is true that

$$\frac{\partial ln a''}{\partial T} = -\frac{\Delta H}{RT^2}. \tag{71a}$$

It is also true that at the freezing point of the solution, since the system is in equilibrium, the activity of the solid equals the activity of the liquid in the solution, or a'' equals a'.

According to equation (68), the activity of the solvent is related to the activity, a_2, of the solute as follows:

$$\partial ln a' = -\frac{N_2}{N_1}\partial ln a_2, \tag{68}$$

and, by substitution in (71a),

$$\partial ln a_2 = \frac{N_1}{N_2}\frac{\Delta H}{RT^2}\partial T.$$

Eliminating T, and the mol fractions, we obtain

$$\partial ln a_2 = \frac{55.5}{c}\frac{(-\Delta H)}{R(T_0 - \theta)^2}\partial\theta.$$

Since θ is small compared with T_0, it may be neglected and hence

$$\partial ln a_2 = \frac{55.5(-\Delta H)}{cRT_0^2}\,\partial\theta. \tag{72}$$

If it be assumed that $(-\Delta H)$ is constant over a range of temperature and equal to 1438 cals., its value at 0°, an error is introduced which invalidates the results at the higher concentrations. In the second place, a_2 is the activity of the solute at the freezing point. If the activity is desired at another temperature (e.g., 25°), a calculation according to equation (62) must be made. These two factors which are negligible in very dilute solutions (up to 0.01 molal), but important in concentrated solutions, involve for their calculation a knowledge of the specific heats of water, ice, the partial heat content of the solute and its variation with the temperature, and the partial heat capacity of the solute.[1] In dilute solutions, these complications may be neglected, and, consequently it is found that $\frac{RT_0^2}{55.5(-\Delta H)}$ equals 1.858°, or the molecular lowering of the freezing point for water. If we denote this fraction λ, equation (72) becomes

$$\partial ln a_2 = \frac{\partial\theta}{\lambda c}\cdot \tag{73}$$

This equation is valid within the experimental error for solutions of electrolytes of concentrations not exceeding 0.05 molal. Since a_2 is equal to $a_+^{\nu_+}a_-^{\nu_-}$ for any electrolyte,

$$\partial ln a_2 = \partial ln a_+^{\nu_+}a_-^{\nu_-} = \nu\partial ln a_\pm = \frac{\partial\theta}{\lambda c}\cdot \tag{74}$$

Dividing by ν, we obtain

$$\partial ln a_\pm = \frac{\partial\theta}{\nu\lambda c}\cdot \tag{75}$$

Lewis and Linhart found that the empirical function

$$\left[\nu\lambda - \frac{\theta}{c}\right] = \beta' c^{\alpha'} \tag{76}$$

is valid in dilute solutions of all electrolytes. β' and α' are empirical constants. If we take the logarithm of both members of this equation, we obtain

$$\log\left[\nu\lambda - \frac{\theta}{c}\right] = \log\beta' + \alpha'\log c. \tag{77}$$

It is then clear that by plotting $\log\left(\nu\lambda - \frac{\theta}{c}\right)$ against $\log c$, straight lines will be obtained from which β' and α' may be evaluated.

[1] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921); Thermodynamics, Chaps. XXIII and XXVII; Randall and Bisson, *J. Am. Chem. Soc.*, **42**, 347 (1920).

By transposing (76), differentiating and dividing by $\nu\lambda c$,

$$\frac{\partial\theta}{\nu\lambda c} = lnc - \frac{\beta'(\alpha'+1)c^{\alpha'-1}}{\nu\lambda}\partial c \tag{78}$$

is obtained. This may be combined with (75) and the definite integral

$$\int_{a_0}^{a} \partial ln a_{\pm} = \int_{c_0}^{c} \partial lnc - \frac{\beta'(\alpha'+1)c^{\alpha'-1}}{\nu\lambda}\partial c$$

formed. When $c_0 = 0$, $a_{\pm_0} = c_0$, whence, upon substitution of $c\gamma$ for $a_{\pm}$, integration, and conversion to common logarithms,

$$\log\gamma = -\frac{\beta'(\alpha'+1)}{2.303\nu\lambda\alpha'}c^{\alpha'} \tag{79}$$

is obtained. Since β', α', ν and λ are constants in case of a given electrolyte in aqueous solution, it is seen that this equation may be written

$$\log\gamma = -\beta c^{\alpha'}, \tag{80}$$

where

$$\beta = \frac{\beta'(\alpha'+1)}{2.303\nu\lambda\alpha'}. \tag{81}$$

Equation (80) will prove very useful in later calculations.

In Fig. 5 is given a characteristic plot [1] of $\log\left(\nu\lambda - \frac{\theta}{c}\right)$ against $\log c$ of the

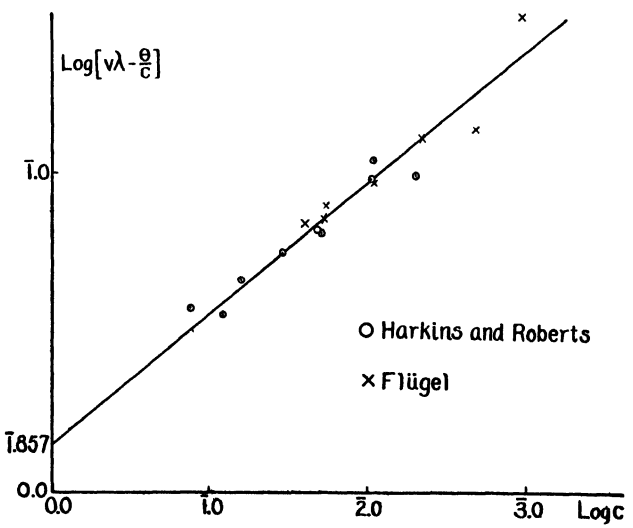


FIG. 5. Freezing Point Data of Dilute Sodium Chloride Solutions

[1] Harned, *J. Am. Chem. Soc.*, **44**, 252 (1922).

combined freezing point data of Flügel,[1] and Harkins and Roberts [2] of dilute sodium chloride solutions. From the straight line drawn through the points, it is found that β' equals 0.720, α' equals 0.413, and, according to equation (81), β equals 0.288.

In Table X are given the values of the constants β', β and α', and the activity coefficients of many electrolytes in dilute solutions obtained by this method. Most of the values were obtained by Lewis and Linhart, but some have been revised by Lewis and Randall. The values for sodium and potassium chlorides are those obtained by Harned. The activity coefficients from 0.0001 to 0.01 molal were computed by equation (79); and at 0.05 and 0.1 molal were computed by the equation which includes the correction caused by the variation of the latent heat of fusion of ice with the temperature. These values may be used at 0° or at 25°, since the temperature variation of activity coefficients of solutions of these dilutions is very small.

TABLE X

ACTIVITY COEFFICIENTS IN VERY DILUTE SOLUTIONS FROM FREEZING POINT DATA

Electrolyte	β'	α'	β	0.0001	0.0005	0.001	0.005	0 01	0.05	0.1
KCl	0.692	0.394	0.286	0.982	0.970	0.961	0.926	0.903	0.821	0.779
NaCl	0.720	0.413	0.288	0.985	0.972	0.963	0.928	0.906	0.834	0.792
KNO_3	1.585	0.565	0.513	0.994	0.984	0.976	0.943	0.916	0.806	0.732
KIO_3, $NaIO_3$	1.548	0.500	0.543	0.99	0.97	0.96	0.915	0.882	0.765	0.692
K_2SO_4	3.187	0.374	0.912	0.935	0.885	0.85	0.75	0.69	0.505	0.421
$BaCl_2$	2.66	0.364	0.776	0.94	0.89	0.865	0.77	0.72	0.568	0.501
$CoCl_2$	2.456	0.362	0.720	0.94	0.90	0.87	0.78	0.73	—	—
$MgSO_4$	5.35	0.38	2.27	0.85	0.75	0.69	0.50	0.40	0.225	0.166
$CdSO_4$	5.35	0.38	2.27	0.85	0.75	0.69	0.50	0.40	0.220	0.160
$CuSO_4$	5.35	0.38	2.27	0.85	0.75	0.69	0.50	0.40	0.216	0.158
$K_3Fe(CN)_6$	8.53	0.42	1.68	0.92	0.85	0.81	0.66	0.57	—	—
$La(NO_3)_3$	8.53	0.42	1.68	0.92	0.85	0.81	0.66	0.57	0.391	0.326

These values are approximations, and rest on fragmentary and difficultly obtainable data. Although subject to revision, they are the best available at the present time for the calculation of the activity coefficients at higher concentrations from electromotive force data.

Activity Coefficients at High Concentrations from Electromotive Force Data: Cells of the type

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{MeX}\ (c_1)\,|\,\mathrm{Me(Hg)}_x\,|\,\mathrm{MeX}\ (c_2)\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag},$$

where $\mathrm{Me(Hg)}_x$ is an alkali metal amalgam, and MeX is an alkaline halide, have been studied very carefully by Allmand and Polack,[3] Pearce and Hart,[4] and especially by MacInnes and his collaborators.[5] Accurate data are now available on such cells containing potassium chloride, sodium chloride, lithium chloride and potassium bromide. In addition, cells of the types

$$\mathrm{Hg}\,|\,\mathrm{HgO}\,|\,\mathrm{KOH}\ (c_1)\,|\,\mathrm{K(Hg)}_x\,|\,\mathrm{KOH}\ (c_2)\,|\,\mathrm{HgO}\,|\,\mathrm{Hg}$$

[1] *Z. physik. Chem.*, **79**, 585 (1912).

[2] *J. Am. Chem. Soc.*, **38**, 2676 (1916).

[3] *J. Chem. Soc.*, **115**, 1020 (1919).

[4] *J. Am. Chem. Soc.*, **43**, 2483 (1921).

[5] MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915). MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920). Beattie, *J. Am. Chem. Soc.*, **42**, 118 (1920).

and

$$H_2|\,KOH\ (c_1)\,|\,K(Hg)_x\,|\,KOH\ (c_2)\,|\,H_2$$

have been studied by Ming Chow,[1] and Knobel,[2] from which the activity coefficients of potassium hydroxide may be computed.

Although measurements of these cells were made at concentrations as low as 0.001 molal, the results cannot be used to extrapolate to zero concentration, nor, at these low concentrations, are the activity coefficients determined from these results consistent with the freezing point data. This point has been illustrated by Table IX. This lack of concordance has been attributed to unavoidable side reactions, which influence the electromotive forces of the cells containing the dilute solutions.[3] At concentrations above 0.03 molal, the agreement with the freezing point and other data is excellent. These data may be used to compute the activity coefficients in concentrated solutions.

If we consider the reaction

$$C^+A^-\ (c_1) = C^+A^-\ (c_2),$$

we have according to (49)

$$\Delta F = \bar{F}_2 - \bar{F}_1 = -\,\mathbf{NEF} = RTln\,\frac{a_+''a_-''}{a_+'a_-'}\cdot \tag{49}$$

A transfer from a dilute to a concentrated solution would be accompanied by an increase in free energy, and, therefore, **E** is positive when c_1 is greater than c_2. Since $a_\pm$ is equal to $(a_+a_-)^{1/2}$ and also to $c\gamma$, we obtain

$$-\,\mathbf{NEF} = 2RTln\,\frac{c''\gamma''}{c'\gamma'} \tag{82}$$

or

$$\mathbf{E} = 0.1183\,\log\frac{c'\gamma'}{c''\gamma''} \tag{83}$$

at 25°. If then γ is known at one concentration, its value may be computed at another concentration.

In Table XI, the activity coefficients of some uniunivalent electrolytes in concentrated solutions have been compiled. These were computed from electromotive force data by means of equation (83). The reference values of γ employed were 0.779, 0.779 and 0.792 at 0.1 molal concentration for potassium chloride, potassium bromide and sodium chloride, respectively, taken from Table X. The values of lithium chloride are the same as calculated by Lewis and Randall from the data of MacInnes and Beattie, and are based on the assumption that the activity coefficient at 0.01 molal concentration is the same, approximately, as that of hydrochloric acid. The activity coefficients of potassium hydroxide have been computed from the data of Knobel.[4]

Further, the activity coefficients of sulphuric acid calculated by Lewis and Randall from electromotive force, vapor pressure, and freezing point data have been included.

[1] *J. Am. Chem. Soc.*, **42**, 488 (1920).
[2] *J. Am. Chem. Soc.*, **45**, 70 (1923).
[3] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).
[4] *J. Am. Chem. Soc.*, **45**, 70 (1923).

TABLE XI

ACTIVITY COEFFICIENTS OF SOME ELECTROLYTES AT HIGH CONCENTRATIONS CALCULATED FROM THE ELECTROMOTIVE FORCE DATA AT 25°

c	γ					
	KCl	KBr	NaCl	LiCl	KOH [4]	H_2SO_4
0.01	0.903	0.903	0.906	0.922	0.920	0.617
0.03	0.851	0.851	0.857	0.864	0.857	—
0.05	0.816	0.816	0.831	0.843	0.822	0.397
0.1	0.779	0.766	0.792	0.804	0.792	0.313
0.2	0.723	0.724	0.745	0.774	0.763	0.244
0.3	0.695	0.692	0.714	0.752	0.748	0.209
0.5	0.659	0.653	0.682	0.754	0.740	0.178
1	0.613	0.597	0.652	0.776	0.775	0.150
2	(0.566)[1]	(0.580)[2]	0.672	(0.936)[3]	—	0.147
3	(0.575)[1]	(0.630)[2]	0.722	1.20	1.136	0.166
4	—	—	(0.794)[3]	—	—	0.203
5	—	—	(0.892)[3]	—	—	0.242
6.12	—	—	1.019 (sat.)	—	—	—

It is clear from this table that at constant temperature the activity coefficients of these electrolytes pass through minimum values at different salt concentrations. In this respect, they are similar to the activity coefficient of hydrochloric acid. The activity coefficients of the uniunivalent chlorides are plotted against the concentration in Fig. 6. It appears from these curves that the activity coefficients are higher in the solutions containing cations of higher hydration values.

Form of the Activity Coefficient-Concentration Function at Constant Temperature and Pressure: Noyes and Falk [5] showed, from the freezing point data at that time available, that in the case of a uniunivalent electrolyte, the equation

$$2 - i = k\sqrt{c}$$

expressed within the experimental error the variation of i, the van't Hoff factor,

[1] Values at 2 and 3 molal were taken from the data of Harned, *J. Am. Chem. Soc.*, **38**, 1986 (1916); **44**, 252 (1922), on measurements of cells with a liquid junction. These measurements give a minimum at about 2.5 molal and in this respect differ from the measurements of the same cell by Getman, *J. Am. Chem. Soc.*, **42**, 1556 (1920). There is other evidence of the presence of a slight minimum which will be discussed when the vapor pressures of these solutions are considered. These values are provisional since they are based on an assumption regarding the transference number.

[2] Conjectural because they are based on a single value at 2.8 molal.

[3] Interpolated graphically.

[4] Probably not so exact as the values for the other electrolytes since they are derived from only one series of measurements.

[5] *J. Am. Chem. Soc.*, **32**, 1011 (1910).

with the concentration in dilute solutions. Bjerrum[1] showed by thermodynamic reasoning that this expression was equivalent to

$$\log \gamma = -\beta\sqrt[3]{c}. \tag{84}$$

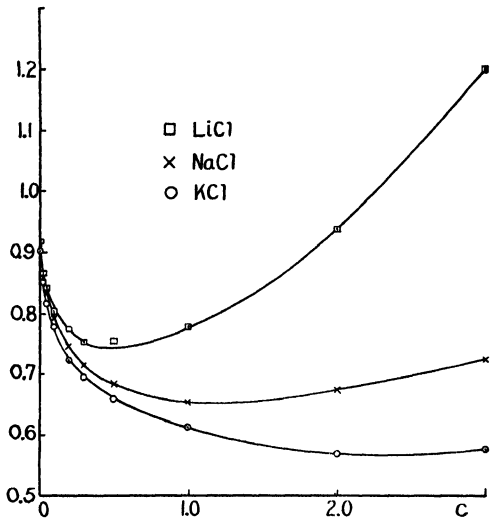


Fig. 6. Activity Coefficients of Uniunivalent Halides

This equation is a particular form of the more general equation (80) which results from Lewis and Linhart's more recent calculation.

In many of the subsequent calculations, chosen for the purpose of illustrating thermodynamic methods, it will be very convenient to employ an equation which expresses the activity coefficient as a function of the molal concentration throughout a considerable concentration range at constant temperature and pressure. A comparatively simple equation which suffices for this purpose with a considerable degree of accuracy and throughout a long concentration range is

$$\log \gamma = \alpha c - \beta c^{\alpha'}, \tag{85}$$

where α, β and α' are constants.[2] The term αc becomes negligible in very dilute solutions, so that this equation approaches (80) as c approaches zero.

A convenient way of evaluating α, β and α' from a given series of results is as follows. By dividing (85) by c and transposing,

$$\left[\frac{-\log \gamma}{c} + \alpha\right] = \beta c^{\alpha'-1}$$

is obtained. Taking the logarithms of both members of this equation, we obtain

$$\log\left[\frac{-\log \gamma}{c} + \alpha\right] = \log \beta + (\alpha' - 1)\log c. \tag{86}$$

It is clear that if the $\log\left[\frac{-\log \gamma}{c} + \alpha\right]$ is plotted against $\log c$, and if α be assigned the correct value, a straight line should be obtained. In practice,

[1] *Z. Elektrochem.*, **24**, 321 (1918); *Z. anorg. Chem.*, **109**, 275 (1920).

[2] Harned, *J. Am. Chem. Soc.*, **42**, 1808 (1920); **44**, 252 (1922).

α may be assigned different values until a straight line is obtained. Other values of α, greater or less than the correct one, will give curves of opposite curvatures. From such a plot, the values of β and α' may easily be obtained. To illustrate this graphical method, which also serves to test the consistency of the data, Table XII has been compiled. Columns (6) and (7) contain the activity coefficients of hydrochloric acid at concentrations corresponding to c, calculated by Lewis and Randall, and Noyes and MacInnes, respectively.

Columns (2), (3), (4) and (5) need no explanation. The plot is given in Fig. 7. The value assigned to α by this method of trial is, in the present

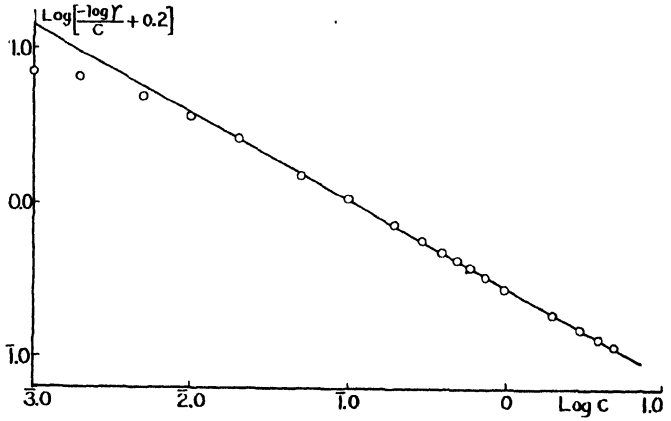


FIG. 7. Plot for Evaluating Constants of Equation (85)

instance, 0.20. With the exception of a few points at concentrations below 0.01 molal, all points lie near the straight line. When c equals unity, log c equals zero, and log β equals $\bar{1}.459$, or β equals 0.288. The slope of the curve is $(\alpha' - 1)$ and is negative, whence $(1 -$ slope$)$ equals α', which, in the present instance, is 0.450. Column (8) contains the values calculated by equation (85), and the agreement of these with the observed values in column (6) is very good considering that the equation has been applied over a concentration range from 0.0005 to 5 molal. The calculated results are higher than the observed at concentrations above 5 molal. Further, through the range of 0.0005 to 5 molal concentrations, the observed values fall alternately above and below the calculated values. In the range from 0.1 to 0.5 molal, the calculated results are higher than those obtained by Lewis and Randall, but lie very close to the values calculated by Noyes and MacInnes[1] from the data of Ellis. Considering this agreement, equation (85) is certainly at least a very useful approximation equation.

That equation (85) is also valid over a considerable concentration for both uniunivalent and unibivalent electrolytes is shown by Table XIII where the observed values of the activity coefficients of lithium chloride, sulphuric acid and sodium chloride, taken from Table XI, are compared with those calculated. The values for the constants α, β and α' are given in Table XIV.

[1] *J. Am. Chem. Soc.*, 42, 239 (1920).

TABLE XII

OBSERVED ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID AT 25° COMPARED WITH VALUES CALCULATED BY EQUATION (85)

c	$\log c$	$\frac{-\log \gamma}{c}$	$\left[\frac{-\log \gamma}{c} + 0.20\right]$	$\log\left[\frac{-\log \gamma}{c} + 0.20\right]$	γ (obs.) (Lewis and Randall)	γ (obs.) (Noyes and MacInnes)	γ (calc.) ($\alpha = 0.20$) ($\beta = 0.288$) ($\alpha' = 0.450$)
0.0005	6.699	7.86	8.06	10 9063	0.991	—	0.979
0.001	7.000	7.00	7.20	10.8573	0.984	—	0.971
0.002	7.301	6.39	6.59	10.8189	0.971	—	0.961
0.005	7.699	4.73	4.93	10.6929	0.947	—	0.943
0.01	8.000	3.43	3.63	10.5599	0.924	0.932	0.924
0.02	8.301	2.43	2.63	10.4200	0.894	—	0.900
0.05	8.699	1.31	1.51	10.1790	0.860	0.855	0.861
0.1	9.000	0.894	1.094	10.0390	0.814	0.823	0.827
0.2	9.301	0.531	0.731	9.8639	0.783	0.796	0.795
0.3	9.477	0.383	0.583	9.7657	0.768	0.783	0.781
0.4	9.602	0.294	0.494	9.6937	0.763	—	0.775
0.5	9.699	0.236	0.436	9.6395	0.762	0.773	0.775
0.6	9.778	0.189	0.389	9.5900	0.770	—	0.778
0.75	9.875	0.1379	0.338	9.5289	0.788	—	0.789
1	10.000	0.0846	0.285	9.4548	0.823	—	0.817
2	10.301	−0.00684	0.1932	9.2860	1.032	—	1.016
3	10.477	−0.0434	0.1566	9.1948	1.35	—	1.343
4	10.602	−0.0662	0.1338	9.1265	1.84	—	1.831
5	10.699	−0.0799	0.1201	9.0795	2.51	—	2.546
6	—	—	—	—	3.40	—	(3.59)
7	—	—	—	—	4.66	—	(5.11)

TABLE XIII

OBSERVED AND CALCULATED VALUES OF ACTIVITY COEFFICIENTS

c	LiCl		H_2SO_4		NaCl	
	γ (obs.)	γ (calc.)	γ (obs.)	γ (calc.)	γ (obs.)	γ (calc.)
0.01	0.922	0.920	0.617	0.606	0.906	0.906
0.03	0.864	0.876	—	—	0.857	0.860
0.05	0.843	0.851	0.397	0.408	0.834	0.832
0.1	0.804	0.812	0.313	0.323	0.792	0.791
0.2	0.774	0.774	0.244	0.247	0.745	0.744
0.3	0.752	0.755	0.209	0.210	0.714	0.716
0.5	0.754	0.743	0.178	0.173	0.682	0.683
1	0.776	0.771	0.150	0.148	0.652	0.652
2	0.936	0.944	0.147	0.175	0.672	0.662
3	1.200	1.237	0.166	(0.269)	0.722	0.712
4	—	—	—	—	0.794	0.789
5	—	—	—	—	0.892	0.890
6.12	—	—	—	—	1.019 (sat.)	1.033

The agreement between the observed and calculated values is good for all three electrolytes. The calculated activity coefficients of sulphuric acid depart from the observed at about 2 molal or 4 weight normal concentration. A similar calculation of the activity coefficients of potassium chloride was made by Harned [1] and the concordance between the observed and calculated values was found satisfactory.

From these considerations and similar ones for other electrolytes, it is found that the above equation is approximately valid for all accurately determined data throughout concentration ranges extending from very dilute solutions to 3 molal concentrations and, in some cases, beyond for uniunivalent electrolytes, and to 3 weight normal concentrations or beyond for unibivalent electrolytes.

Table XIV contains the values of α, β and α' for the electrolytes thus far considered. These are the values at 25° unless otherwise specified. The tested range of validity is also given.

TABLE XIV

VALUES OF CONSTANTS OF EQUATION (85)

Electrolyte	Range of Validity	α	β	α'
HCl	0.005–6	0.20	0.288	0.450
LiCl	0.01–3	0.21	0.323	0.463
NaCl	0.01–6.12	0.10	0.286	0.407
KCl	0.01–3	0.07	0.292	0.396
KBr	0.01–3	0.07	0.292	0.396
KOH	0.01–1	0.18	0.288	0.387
KNO_3	0.001–0.1	(0.07)	0.513	0.565
KIO_3, $NaIO_3$	0.001 0.1	(0.07)	0.543	0.500
$AgNO_3$ (0°)	0.01–5	—	(0.406)	(0.470)
K_2SO_4	0.001–0.1	—	0.912	0.374
H_2SO_4	0.01–2	0.47	1.30	0.383
$BaCl_2$	0.001–0.01	—	0.776	0.364
$CoCl_2$	0.001–0.01	—	0.720	0.362
$MgSO_4$	0.001–0.01	—	2.27	0.38
$CdSO_4$	0.001–0.01	—	2.27	0.38
$CuSO_4$	0.001–0.01	—	2.27	0.38
$K_3Fe(CN)_6$	0.001–0.01	—	1.68	0.42
$La(NO_3)_3$	0.001–0 01	—	1.68	0.42

Owing to the short ranges of concentrations over which the activity coefficients of some of these electrolytes are known, no attempts have been made to evaluate all the constants. The values of α in brackets for potassium nitrate and iodate are provisional. The activity coefficient of silver nitrate computed by Lewis and Randall may be approximately calculated by the use of the values of β and α'.

There is much more concordance between the α' values of the different electrolytes than between the values of the other constants. The β constants are different for electrolytes of different valence types. The β and α' constants are nearly alike for the first six uniunivalent electrolytes, whereas the values of

[1] *J. Am. Chem. Soc.*, **44**, 252 (1922).

α, which become of great importance in concentrated solutions, differ, and this difference seems to be in the direction of the ionic hydration values of the cations. A hydration theory will be considered in another section.

These constants have in the main been derived from rather fragmentary experimental data, and therefore the values of β and α' do not fulfill the theoretical requirement that the activity coefficients of all electrolytes of the same valence type approach unity uniformly as the concentration approaches zero. Lewis and Randall suggested as an empirical rule that for uniunivalent electrolytes α' equals $\frac{1}{2}$. Brönsted,[1] from other considerations involving the Milner theory of electrolytes, employed the equation $\log \gamma = -0.42c^{1/2} + \alpha c$ for dilute solutions of uniunivalent electrolytes. $\log \gamma = -0.42c^{1/2}$ is thus made a universal limiting function. That $\log \gamma = -\beta c^{1/2}$ would follow from Milner's theory has been shown by Cavanaugh.[2] More recently, Debye and Hückel [3] have obtained a universal limiting function which for all electrolytes becomes

$$\log \gamma = -0.351 w \sqrt{\nu c}$$

in extremely dilute aqueous solutions at 0° C., and in which w is a valence factor given by

$$w = \left(\frac{\Sigma \nu_i z_i^2}{\Sigma \nu_i} \right)^{3/2},$$

where ν_i is the number of ions of the ith kind produced by dissociation of one molecule of electrolyte, and z_i is the valence of the ith ion. ν is equal to $\Sigma \nu_i$.

The values of β in Table XIV are all lower than predicted by Debye and Hückel's theory with the exception of those for potassium nitrate and the iodates. Indeed, the available freezing point data are too fragmentary and not of a sufficient degree of accuracy in the very dilute solutions to confirm this law exactly. According to their equation, β should be 0.495, 1.72, 3.65, and 3.97 for uniunivalent, biunivalent, triunivalent, and bibivalent electrolytes, respectively, which values are roughly 1.5 to 2.0 times greater than those in the table. In general, it can only be shown that the available freezing-point data seem to approach conformity to their law as the concentration approaches zero. Fortunately, much more accurate evidence for the validity of this law has been obtained by Brönsted and La Mer [4] from solubility data. Further discussion of Debye and Hückel's theory will be presented in a later section.

As a result of this discussion and the laborious calculations just reviewed, it can be said that the activity coefficients of all electrolytes can be expressed as a function of the concentration at constant temperature and pressure and over a wide concentration range by a single equation. The present available activity coefficients at 25° have been organized in such a way that they may

[1] Brönsted, *J. Am. Chem. Soc.*, **44**, 938 (1922).
[2] Cavanaugh, *Phil. Mag.*, **43**, 606 (1922); **44**, 226 (1922); **44**, 610 (1922).
[3] Debye and Hückel, *Physik. Z.*, No. 9, 185 (1923).
[4] Brönsted and La Mer, *J. Am. Chem. Soc.*, **46**, 555 (1924).

be calculated with a considerable but undetermined degree of accuracy b equation (85) and a table of constants. This equation is introduced for th purpose of facilitating further calculations.

THE ACTIVITY COEFFICIENT AND OTHER COLLIGATIVE PROPERTIES. GENERA. CONSIDERATIONS RELATING TO SOLUTION THEORY

The Activity of a Volatile Component and its Vapor Pressure: When a volatile component of a solution is in equilibrium with its vapor, the activity of the component in the solution, a_1, is equal to its activity in the vapor state a_v, and, according to equation (56),

$$\partial \overline{F}_1 = RT\partial ln a_1 = RT\partial ln a_v. \tag{56}$$

From the law of dilute systems, and the definition of activity, it immediately follows that the gas laws hold for the dilute vapor, and that a_v is proportional to the concentration and also to the pressure of the vapor, p_1, in dilute gases. In general, then, for a volatile component, at pressure ranges where the gas laws are valid for the vapor,

$$\partial \overline{F}_1 = RT\partial ln p_1, \tag{87}$$

and, in case of a second volatile component,

$$\partial \overline{F}_2 = RT\partial ln p_2. \tag{87}$$ [1]

It has previously been shown that the activities of two components in a solution at constant pressure and temperature are related by

$$N_1\partial ln a_1 + N_2\partial ln a_2 = 0. \tag{68}$$

If both are volatile,

$$N_1\partial ln p_1 + N_2\partial ln p_2 = 0$$

is obtained, an equation originally derived by Duhem [2] which is valid for the range of vapor pressures over which the law of the ideal gas holds. Equation

[1] Another treatment of this subject may be made by employing the fugacity function, f. This function could here be defined by the equation

$$f = aRT$$

and is related to the pressure in the same way the activity is related to the concentration. Indeed, in Lewis and Randall's system of thermodynamics, the fugacity or escaping tendency is defined first and the relative activity defined as equal to the relative fugacity or (f/f_0). Equations (87) are thus limiting laws, which rest on the validity of the gas laws when applied to the vapor. They are valid within the experimental error for all calculations which follow. The general law would be

$$\partial \overline{F}_1 = RT\partial ln a_1 = RT\partial ln \frac{f_1}{f_0}.$$

Since, up to the present, the fugacity has been employed very little in solution thermodynamics, it has been omitted in the present discussion.

[2] *Compt. rend.*, **102**, 1449 (1886).

(68) permits the calculation of the activity of the volatile component from its vapor pressure, and also the activity of the volatile component from the activity of the non-volatile component.

Let us now consider the transfer of a mol of the volatile component from the solution to pure solvent, and let $\overline{F}_0$, a_0, p_0 refer to the partial free energy, activity and vapor pressure of the solvent, respectively. This change will be accompanied by a decrease in free energy, and consequently, according to (56) and (87),

$$(-\Delta\overline{F}) = -(\overline{F}_1 - \overline{F}_0) = RTln\frac{a_0}{a_1} = RTln\frac{p_0}{p_1}. \qquad (88)$$

Let the activity of the pure component equal unity, whence $\overline{F}_0$ will equal zero, a_1 will be the relative activity, and

$$\overline{F}_1 = RTlna_1 = RT\int_{p_0}^{p_1} \partial lnp = RTln\frac{p_1}{p_0}. \qquad (89)$$

Employing these conventions, the relative activity is equal to the ratio of the vapor pressure of the component in the solution to the vapor pressure of the pure component.

Calculation of the Activity Coefficient of the Solute from its Partial Vapor Pressure: In general, the activity of a component in a solution is directly proportional to its vapor pressure. A direct verification of this principle may be obtained from the results of Bates and Kirschmann [1] who measured the partial vapor pressure of hydrogen chloride above aqueous solutions of concentrated hydrochloric acid. Since the partial vapor pressure of the acid, p, is proportional to a_2, the activity of the acid, $\frac{p^{1/2}}{c}$ will be proportional to $\frac{a_2^{1/2}}{c}$ or γ, the mean activity coefficient. If γ is assigned the same value at 4 molal as determined by the electromotive force method, the proportionality factor may be determined, and γ calculated at the other concentrations. This calculation has been made by Lewis and Randall [2] and their results are given in Table XV. The proportionality factor was found to be 0.000664.

With the exception of the result at 10 molal concentration, the agreement is excellent. Vapor pressure measurements may, accordingly, be of considerable value for the determination of activity coefficients in very concentrated solutions.

Calculation of the Activity Coefficient of the Solute from the Partial Vapor Pressure of Solvent: By rearranging equation (68), and letting a_1 equal the activity of the solvent and a_2 the activity of the solute, the equation

$$\partial lna_2 = -\frac{N_1}{N_2}\partial lna_1 \qquad (68a)$$

[1] *J. Am. Chem. Soc.*, **41**, 1991 (1919).
[2] *J. Am. Chem. Soc.*, **43**, 1112 (1921).

TABLE XV

COMPARISON OF THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID FROM ELECTROMOTIVE FORCE AND VAPOR PRESSURE DATA

c	p (mm.)	γ (E.M.F.) (Table XII)	γ (V.P.)
4	0.0182	1.84	1.84
5	0.0530	2.51	2.51
6	0.140	3.40	3.41
7	0.348	4.66	4.60
8	0.844	6.30	6.27
9	1.93	8.32	8.43
10	4.20	10.65	11.20

is obtained. a_1, the relative activity referred to pure solvent, has been shown to equal $\frac{p_1}{p_0}$, where p_1 is the vapor pressure of the solvent over the solution, and p_0 is the vapor pressure of pure solvent. Substituting this value for a_1 in equation (68a) and forming the integral, we obtain

$$\int \partial ln a_2 = -\int \frac{N_1}{N_2} \partial ln \frac{p_1}{p_0} . \tag{90}$$

Since sufficiently accurate measurements of the vapor pressure cannot be made at low concentrations so that the activity coefficient of the solute may be determined, this equation is only useful for the most part in determining activity ratios. To this end, the definite integral

$$\int_{a_2'}^{a_2''} \partial ln a_2 = -\int_{p_1'}^{p_1''} \frac{N_1}{N_2} \partial ln \frac{p_1}{p_0} \tag{91}$$

may be employed. By plotting $\frac{N_1}{N_2}$ against $ln \frac{p_1}{p_0}$ and evaluating the area between the limits graphically, the definite integral may be obtained. The negative of this integral equals $ln \frac{a_2''}{a_2'}$.[1]

Calculation of the Vapor Pressure and Activity of the Solvent from the Activity of the Solute: The vapor pressure of the solvent at all concentrations of solute may be accurately calculated by the same method. In this case, the definite integral may be employed in the form

$$\int_{p_0}^{p_1} \partial ln p_1 = -\int_0^{a_2} \frac{N_1}{N_2} \partial ln a_2 \tag{92}$$

[1] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921)—Table III.

and by plotting $\frac{N_1}{N_2}$ against lna_2 and integrating graphically, the negative of $ln\frac{p_1}{p_0}$ is obtained, or $ln\frac{p_0}{p_1}$.

It is clear that if a_2 is known as a function of $\frac{N_1}{N_2}$, the above equation may be integrated, and an analytical expression obtained for $ln\frac{p_0}{p_1}$. This may be accomplished in the case of solutions of electrolytes by employing the equation

$$\log \gamma = \alpha c - \beta c^{\alpha'} \tag{85}$$

or any other equation which expresses γ as a function of c at constant pressure and temperature. The result of this operation will be as exact as the equation employed. This method, if equation (85) is employed, will give a very convenient, although approximate, result, for calculating the activity and vapor pressure of water in aqueous solutions of all the electrolytes whose α, β and α' constants are given in Table XIV.

According to equations (51) and (85), we obtain

$$\log \gamma = \log \frac{a_{\pm}}{c(\nu^{+\nu^+}\nu^{-\nu^-})^{1/\nu}} = \alpha c - \beta c^{\alpha'}, \tag{51, 85}$$

where

$$a_{\pm} = (a_+^{\nu^+}a_-^{\nu^-})^{1/\nu}$$

and

$$lna_{\pm} = \frac{1}{\nu} lna_+^{\nu^+}a_-^{\nu^-}.$$

Converting the first of these equations to natural logarithms and rearranging, we obtain

$$lna_+^{\nu^+}a_-^{\nu^-} = \nu\left(2.303\alpha c - 2.303\beta c^{\alpha'} + lnc + \frac{1}{\nu} ln\nu^{+\nu^+}\nu^{-\nu^-}\right),$$

which upon differentiation becomes

$$\partial lna_+^{\nu^+}a_-^{\nu^-} = \nu(2.303\alpha\partial c - 2.303\beta\alpha' c^{\alpha'-1}\partial c + \partial lnc). \tag{93}$$

Now, according to equation (68), if a_1 is the activity of the water molecule in a solution of an electrolyte,

$$\partial lna_1 = -\frac{N_2}{N_1}\partial lna_+^{\nu^+}a_-^{\nu^-}. \tag{68b}$$

Further

$$N_2 = \frac{c}{55.5 + c}; \qquad N_1 = \frac{55.5}{55.5 + c}$$

and

$$\frac{N_2}{N_1} = \frac{c}{55.5}. \tag{94}$$

Combining (68*b*), (93) and (94), we obtain

$$-\partial ln a_1 = \frac{\nu c}{55.5}(2.303\alpha\partial c - 2.303\beta\alpha' c^{\alpha'-1}\partial c + \partial lnc).$$

a_1 is proportional to p_1, and if we let p_0 equal the vapor pressure when c equals zero, or the vapor pressure of the pure solvent, the definite integral

$$-\int_{p_0}^{p_1} \partial ln p_1 = \int_0^c \frac{\nu c}{55.5}(2.303\alpha\partial c - 2.303\beta\alpha' c^{\alpha'-1}\partial c + \partial lnc)$$

may be constructed, which upon integration becomes

$$ln\frac{p_0}{p_1} = \frac{c}{55.5}\left[\nu + \frac{2.303\alpha\nu c}{2} - \frac{2.303\nu\beta\alpha'}{\alpha'+1}c^{\alpha'}\right]. \tag{95}$$

For a uniunivalent electrolyte, ν equals two and

$$ln\frac{p_0}{p_1} = \frac{c}{55.5}\left[2 + 2.303\alpha c - \frac{4.606\beta\alpha'}{\alpha'+1}c^{\alpha'}\right]. \tag{96}$$

The term within the brackets is recognized to be van't Hoff's factor, i, and equations (95) and (96) may be written

$$ln\frac{p_0}{p_1} = \frac{c}{55.5}[i]. \tag{97}$$

As a result of these deductions, van't Hoff's factor, the vapor pressures of solutions of many electrolytes, and the activity of the water molecule may be computed by introducing into the above equations the values of α, β and α' given in Table XIV. These values were obtained from the most accurate data available and, consequently, the vapor pressures computed by this method will be more accurate than those obtained by direct measurement, particularly in dilute solutions. The method of deduction is general, although the accuracy in the present case depends on the validity of the empirical equation employed.

For the sake of comparison, it is convenient to employ the function, $\left(\frac{i-1}{\nu-1}\right)$, which in the classic theory of solutions was often considered to equal the degree of dissociation. Let this factor, for purposes of characterization, be called the van't Hoff coefficient, and be denoted by γ_0.[1] For a uni-

[1] It is preferable to give this factor a name and a symbol in order to differentiate it, on the one hand from the conductance ratio, Λ/Λ_0, and, on the other hand, from the osmotic coefficient, ϕ, introduced by Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918), and sometimes employed by Brönsted, *J. Am. Chem. Soc.*, **42**, 761 (1920); **44**, 877 (1922); **44**, 938 (1922). This latter quantity is equal to i/ν. The more familiar γ_0 will be employed.

univalent electrolyte

$$\gamma_0 = 1 + \alpha'' c - \beta'' c^{\alpha'}, \tag{98}$$

where

$$\alpha'' = 2.303\alpha \tag{99}$$

and

$$\beta'' = \frac{4.606\beta\alpha'}{\alpha' + 1}. \tag{100}$$

By means of equation (98) and these latter two relations, it is a comparatively simple matter to evaluate the constants α, β and α' from a knowledge of γ_0. By transposing (98), and taking the logarithms of both members, we obtain

$$\log [1 - \gamma_0 + \alpha'' c] = \log \beta'' + \alpha' \log c.$$

By plotting the left member of this equation against log c, and assigning values to α'' until a straight line is obtained, all of these constants may be evaluated, and also α, β and α' by equations (99) and (100). By employing the van't Hoff coefficient data given in Noyes and Falk's compilation,[1] the activity coefficients of many electrolytes, which have not been mentioned in the present discussion, may be approximately computed.

van't Hoff's Coefficient of Potassium Chloride: Lovelace, Frazer, and Sease [2] have carefully determined the vapor pressures of potassium chloride solutions at 20°, and the van't Hoff coefficient, γ_0, has been computed directly from these data by using equation (97). Their best values are given in the third column of Table XVI. The second column contains values of γ_0 calculated by means of equation (98) which becomes

$$\gamma_0 = 1 + 0.1612c - 0.3815c^{0.396}$$

upon substitution of the values of α, β and α'. Values at 0° calculated by Lovelace, Frazer and Sease from freezing point data have been included in the fourth column.[3]

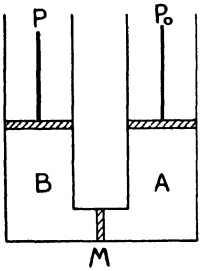


FIG. 8

At the lower concentrations the values agree as well as could be expected. At the higher concentrations, the values are higher at the higher temperatures. Harned has pointed out that a difference of this magnitude and sign would be expected. It is also important to note that minimum values in each case occur at about the same concentration, 1 molal.

Calculation of Osmotic Pressure: In the accompanying diagram (Fig. 8), A is a compartment containing pure solvent separated by a semipermeable membrane, M,

[1] *J. Am. Chem. Soc.*, **34**, 454 (1912).
[2] *J. Am. Chem. Soc.*, **43**, 102 (1921).
[3] Harned, *J. Am. Chem. Soc.*, **49**, 252 (1922).

TABLE XVI

VAN'T HOFF COEFFICIENTS OF POTASSIUM CHLORIDE AT 25°, 20°, AND 0°

c	γ_0 (25°) (E.M.F.)	γ_0 (20°) (V.P.)	γ (0°) (F.P.)
0.001	0.976	—	—
0.01	0.940	—	—
0.05	0.892	0.885	0.891
0.1	0.863	0.846	0.857
0.3	0.812	0.799	0.810
0.5	0.791	0.790	0.794
0.75	0.781	0.786	0.762
1	0.780	0.788	0.748
1.5	0.792	0.794	0.764
2	0.820	0.823	0.763
2.5	0.855	0.844	0.765
3	0.894	0.868	0.805

from a compartment, B, containing the solution. Let the whole system be at constant temperature. Let P and P_0 be pressures such that the system is kept in equilibrium. The osmotic pressure, π, is defined by the difference in these pressures, or $(P - P_0)$. Thus, in compartment A, the solvent will be at a pressure P_0, and, in compartment B, the solvent in the solution will be at a pressure P.

Let us consider a process whereby a mol of solvent is reversibly transferred from the solvent to the solution through the osmotic membrane, and, as in the previous cases, let $\overline{F}_0$ and a_0 equal the partial free energy and activity of the pure solvent at an external pressure, P_0. The partial free energy and activity of the solvent in the solution at an external pressure P will also equal $\overline{F}_0$ and a_0, respectively, under the stipulated conditions of equilibrium. The free energy increment of such a process is zero. Let us now change the pressure on the solution from P to P_0. The change in activity of the solvent caused by this change in pressure may be found by equation (67) which is

$$\left[\frac{\partial ln a}{\partial p}\right]_T = \frac{\overline{V}_1}{RT}, \tag{67}$$

where $\overline{V}_1$ is the partial molal volume of the solvent. Rearranging this equation and forming the definite integral, we obtain

$$\int_{\overline{F}_0}^{\overline{F}_1} \partial \overline{F} = RT \int_{a_0}^{a_1} \partial ln a = \int_{P}^{P_0} \overline{V}_1 \partial P, \tag{101}$$

where a_1 is the activity of the solvent in the solution at a pressure P_0. This equation is exact. If we neglect the change in $\overline{V}_1$ produced by a change in pressure, (the compressibility) $\overline{V}_1$ will equal the molal volume of the solvent V_0. Since the partial free energy of the pure solvent is zero, a_0 will equal unity, and

$$\overline{F}_1 = RTln a_1 = -\overline{V}_1(P - P_0) = -\pi V_0 \tag{102}$$

is obtained. If this equation be combined with (89), we obtain the well-known but approximate law

$$\pi = \frac{RT}{V_0} ln \frac{p_0}{p_1}, \tag{103}$$

which relates the osmotic pressure of the solution to the vapor pressure of the solvent. Combining (103) and (97), we obtain

$$\pi = \frac{RT}{V_0} \frac{c}{55.5} [i], \tag{104}$$

which at 25° reduces to

$$\pi = 24.42c[i], \tag{104a}$$

where π is in atmospheres.

Conductance Ratios, Activity Coefficients, and van't Hoff's Coefficients: For convenience of comparison, the following tables containing the conductance ratios, activity coefficients, and van't Hoff coefficients have been prepared. The conductance ratios have been taken from the tables of Noyes and Falk,[1] the activity coefficients from Tables XI and XII, and the van't Hoff coefficients have been calculated by using equation (97) and the values of α, β and α' in Table XIV. Table XVII contains the values of these coefficients for some uniunivalent electrolytes at different concentrations.

TABLE XVII

CONDUCTANCE RATIOS, VAN'T HOFF COEFFICIENTS, AND ACTIVITY COEFFICIENTS OF SOME UNIUNIVALENT ELECTROLYTES AT 25°

	c	0.01	0.05	0.1	0.5	1	2	3
KCl	Λ/Λ_0	0.941	0.889	0.860	0.779	0.742	—	—
	γ_0	0.940	0.892	0.863	0.791	0.780	0.820	0.894
	γ	0.903	0.816	0.779	0.659	0.613	0.566	0.575
NaCl	Λ/Λ_0	0.936	0.882	0.852	0.773	0.741	—	—
	γ_0	0.944	0.899	0.874	0.828	0.849	0.955	1.096
	γ	0.906	0.834	0.792	0.682	0.652	0.672	0.722
HCl	Λ/Λ_0	0.972	0.944	0.925	0.890	0.845	—	—
	γ_0	0.952	0.916	0.900	0.929	1.049	1.359	1.707
	γ	0.924	0.861	0.827	0.775	0.817	1.016	1.343
LiCl	Λ/Λ_0	0.932	0.878	0.846	0.766	0.737	—	—
	γ_0	0.949	0.906	0.886	0.900	1.012	1.318	1.667
	γ	0.922	0.843	0.804	0.754	0.776	0.936	1.20

In general, the van't Hoff coefficient approaches the conductance ratio as the dilution increases, and in dilute solution is much more nearly equal to this quantity than to the activity coefficient. Table XVIII also contains values of these coefficients obtained from the same sources for electrolytes of many different types at 0.01 molal concentration.

[1] *J. Am. Chem. Soc.*, **34**, 454 (1912).

TABLE XVIII

CONDUCTANCE RATIO, VAN'T HOFF COEFFICIENTS AND ACTIVITY COEFFICIENTS OF SOME ELECTROLYTES AT 0.01 M CONCENTRATION AND 25°

Electrolyte	Λ/Λ_0	γ_0	γ
HCl	0.972	0.952	0.924
LiCl	0.932	0.949	0.922
NaCl	0.936	0.944	0.906
KCl	0.941	0.940	0.903
KNO_3	0.935	0.937	0.916
$NaIO_3$	0.917	0.918	0.882
$BaCl_2$	0.850	0.866	0.72
K_2SO_4	0.832	0.842	0.69
$MgSO_4$	0.596	0.50	0.40
$CdSO_4$	0.534	0.50	0.40
$CuSO_4$	0.550	0.50	0.40
$K_3Fe(CN)_6$	0.778	0.781	0.57
$La(NO_3)_3$	0.75	0.781	0.57

The agreement between the values of $\frac{\Lambda}{\Lambda_0}$ and γ_0 at this dilution is good, considering the difficulties in obtaining the data from which the values of γ_0 were computed. The question of the significance of such an agreement is indeed a difficult one since all these quantities approach unity as the solutions approach infinite dilution. The activity coefficients are much lower than the van't Hoff coefficients even in these dilute solutions. Lewis and Randall [1] have pointed out the interesting rule, which follows from equations (85) and (100), and the assumption that α' equals 0.5, that, in any very dilute solutions of uniunivalent electrolytes, the van't Hoff coefficients differ from unity by two thirds as much as the activity coefficients.

Theoretical Considerations of These Quantities: van't Hoff introduced the factor i in the equation which expressed the abnormal freezing point lowering of solutions of electrolytes. Arrhenius recognized that only those solutions which possessed an i factor greater than unity conducted the electric current. As a result, he suggested that electrolytes were dissociated into ions, and that i was a measure of the number of gram ions and molecules which resulted from the dissociation of a mol of electrolyte. On this theory, if the process of ionization is a partial dissociation of a molecule into ions, γ_0 is a degree of dissociation. Arrhenius moreover suggested that the degree of dissociation may also, from certain further assumptions, be calculated from conductance measurements. It is a matter of considerable importance that in recent years issue has been taken with the classic theory of dissociation by numerous investigators.

In order to measure the number of ions in a solution, we turn first to the electrical conductance. According to the ionic theory, the ions alone are the

[1] *J. Am. Chem. Soc.*, **43**, 1112 (1921).

carriers of electricity. If U_c and U_a are the mobilities of the cation and anion, respectively, the equivalent conductance, Λ, will be $\alpha\mathbf{F}(U_c + U_a)$, where α is the degree of dissociation. At infinite dilution, α equals unity and the equivalent conductance, Λ_0, equals $\mathbf{F}(U_c + U_a)$. Thus, $\frac{\Lambda}{\Lambda_0}$ will equal the degree of dissociation, or, more generally, the fraction of 1 gram equivalent existing as ions which are free to move through the solution at any concentration, on the assumption of Kohlrausch that the mobilities of the ions do not change with the concentration. Kohlrausch's assumption was first questioned by Jahn,[1] and more recently by Lewis [2] and others. Examination of these data shows that, when the transference number of an ion differs considerably from 0.5, it changes materially with a change in concentration. It is probable, therefore, that the ion mobilities vary with the concentration. The nature of this variation is not known; in fact, it is not known whether the mobilities increase or decrease with an increase in concentration. If the mobilities change, $\frac{\Lambda}{\Lambda_0}$ will not be the true degree of dissociation. Instead of Kohlrausch's assumption, Lewis proposes that, in dilute solutions of any two salts with a common ion, at the same concentration, the common ion has the same mobility. Then, the degrees of dissociation for two salts with a common anion would be, respectively,

$$\alpha = \frac{\Lambda}{U_c + U_a}; \qquad \text{and} \qquad \alpha' = \frac{\Lambda'}{U_c' + U_a}.$$

Their ratio, after the introduction of the transference numbers, becomes

$$\frac{\alpha}{\alpha'} = \frac{\Lambda n_a}{\Lambda' n_a'},$$

where n_a and n_a' are the anion transference numbers of the two solutions. By this equation, the ratios of two so-called "corrected degrees" of dissociation may be obtained without a knowledge of absolute ionic mobilities. Lewis calculated this ratio for many uniunivalent salts at 0.1 molal concentration to potassium chloride at 0.1 molal concentration and found that for many salts it differed little from unity. Thus, for hydrochloric acid, sodium, potassium, and lithium chlorides, $\frac{\alpha}{\alpha_{KCl}}$ varied only from 0.992 to 1.000 while the conductance ratios vary from 0.930 to 1.016. Since the $\frac{\alpha}{\alpha_{KCl}}$ ratios were more nearly the same as the activity coefficient ratios of two electrolytes, Lewis was led to regard the activity coefficient as more closely related to the "true" degree of dissociation in dilute solutions than the van't Hoff coefficient. The activity coefficient cannot be a degree of dissociation at higher concentrations since for

[1] *Z. physik. Chem.*, **33**, 545 (1900).
[2] *J. Am. Chem. Soc.*, **34**, 1631 (1912).

some electrolytes it reaches values many times unity.[1] As a result of these considerations, Lewis has abandoned the van't Hoff coefficient as a measure of a degree of dissociation. At the present time, it is safest to regard all three of these coefficients as separate quantities, and any equality or proportionality as limited to very dilute solutions.

There is one further difficulty encountered when the temperature coefficients of either the van't Hoff coefficient or the activity coefficient are considered. If the relative partial heat content of the electrolyte is positive, the activity coefficient as well as the van't Hoff coefficient will decrease with increase in temperature. This conclusion follows from equation (62). The opposite is true when the relative partial heat content of the electrolyte is negative. For example, $\bar{L}_2$ for hydrochloric acid is positive and for sodium chloride is negative (Table VII) It has been found that for all solutions of strong electrolytes, $\frac{\Lambda}{\Lambda_0}$ decreases with a rise in temperature.[2]

In regard to the conductance ratio, nearly all investigators are agreed that all the electricity which passes through the solution is carried by the ions, and that the conductance depends on the mobilities, the charge, and the number of ions which move. $\frac{\Lambda}{\Lambda_0}$, if corrected for change in mobility of the ions with the concentration, would then measure the fraction of the electrolyte changed into "free" ions. Granting the above assumptions, the conductance ratio has a definite significance independent of any hypotheses regarding how these "free" ions are produced, and the condition of the remainder of the electrolyte.

On the other hand, it is a problem of great interest to calculate the conductance ratio and the thermodynamic coefficients from some more fundamental knowledge of the structure of the solution. For many years, doubt has been raised as to whether any truly undissociated molecule exists in a solution of a strong electrolyte. Sutherland [3] was the first to adopt a theory of complete dissociation. Noyes [4] suggested an hypothesis of complete ionization but not complete dissociation for strong electrolytes, by which is meant that the ions which are not "free ions" are bound to ions of the opposite sign by electrostatic forces. More recently, many investigators [5] have supported a similar theory. The fraction of the total number of ions which are "free," or $\frac{\Lambda}{\Lambda_0}$, is a function of their energy and the electrostatic force of attraction which tends to hold them bound in some way. A general development of this theory

[1] γ for 16 molal hydrochloric acid is 43.2.

[2] See Kraus, Properties of Electrically Conducting Systems, American Chemical Society Monograph. Chemical Catalog Co., p. 151.

[3] *Phil. Mag.*, (6) **3**, 161 (1902); **7**, 1 (1906).

[4] Congress Arts Sci. St. Louis Exposition, **4**, 317 (1904).

[5] Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918); *Z. anorg. Chem.*, **109**, 275 (1920); Milner, *Phil. Mag.*, (6) **23**, 551 (1912); **25**, 743 (1913); **35**, 352 (1918); Sutherland, *Phil. Mag.*, **35**, 214, 354 (1918); Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707 (1918); Noyes and MacInnes, *J. Am. Chem. Soc.*, **42**, 239 (1920), etc.

was made by Ghosh, who succeeded in deducing an equation which at least gives the right order of magnitude of the conductance ratio for many electrolytes in many solvents. Ghosh's theory is unsatisfactory because the equation deduced is not within the error of experiment in the dilute solutions. For this and other reasons, this theory has been severely criticized.[1] Many of the shortcomings of Ghosh's theory are overcome by the theory now to be discussed which is most probably the nearest approach to a valid solution of the problem of the behavior of dilute solutions of strong electrolytes.

The Theory of Debye and Hückel: The theory of Debye and Hückel was presented in two papers, of which the first[2] contained the deduction of the equations for calculating the thermodynamic coefficients, and the second[3] contained the discussion of the electrical conductance of strong electrolytes. Only the fundamental assumptions and an outline of the mathematical treatment of the first of these contributions will be presented in the following discussion.

Let us reconsider equation (44) which defines the relative activity and equation (54) which expresses the law of an ideal solute. These are

$$\overline{F} = RT\ ln\ a + \overline{F}_o \tag{44}$$

and

$$\overline{F} = RT\ ln\ c + \overline{F}_o. \tag{54}$$

It is known that, in dilute solutions, equation (54) is almost exactly valid for an undissociated solute but is not valid for an electrolyte. The latter departure from validity is therefore due to ionization. This fact suggests that the partial free energy of an electrolyte may be divided into two parts, $\overline{F}_k$, the part associated with thermal free energy, and $\overline{F}_e$, the part associated with the electrical free energy and nothing else. Thus, $\overline{F}$, the free energy of the electrolyte, would be given by

$$\overline{F} = \overline{F}_k + \overline{F}_e = RT\ ln\ c + \overline{F}_e + \overline{F}_o.$$

From this point of view, if $\overline{F}_e$ can be computed from fundamental considerations regarding the nature of electrolytic solutions, $\overline{F}$ may be obtained and the problem solved.

It is by just such a procedure that Debye and Hückel have made their calculation. They, however, have employed the functions defined by

$$G = S - U/T \tag{i}[4]$$

[1] Kraus, *J. Am. Chem. Soc.*, **43**, 2514 (1921); Kendall, *J. Am. Chem. Soc.*, **44**, 717 (1922); Arrhenius, *Z. physik. Chem.*, **100**, 9 (1922).

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[3] Debye and Hückel, *Physik. Z.*, **24**, 305 (1923). For further discussion of this theory, see Noyes, *J. Am. Chem. Soc.*, **46**, 1080, 1098 (1924).

[4] To avoid confusion, we shall employ Debye and Hückel's symbols and denote their equations by lower case Roman numerals.

and

$$\Phi = G - pv/T.^1 \tag{ii}$$

It is further shown that

$$\Phi_e = G_e = \int \frac{U_e}{T^2} dT. \tag{iii}$$

Also, using this system of nomenclature, equation (54) becomes

$$\Phi_k = \sum_0^s N_i(\phi_i - k \log c_i), \tag{iv}$$

where N_0, $N_1 \cdots N_i \cdots N_s$ are the number of individual species of which the ith kind possesses a value of $\phi = \phi_i$. According to equation (iii), if the electrical energy, U_e, is known, Φ_e may be computed and, when added to Φ_k, gives the total thermodynamic potential required for the calculation of the colligative properties. The problem then is resolved into the difficult calculation of the electrical energy.

At first glance, it would appear that the potential energy of one ion with respect to another of opposite sign or the measure of the work necessary to separate them would be

$$-\frac{1}{D}\frac{\epsilon^2}{r},$$

where $+\epsilon$ and $-\epsilon$ are their charges, D the dielectric constant, and r is the mean distance between the ions. N molecules of a uniunivalent electrolyte would then dissociate into $2N$ ions, and the equation

$$r = (V/2N)^{1/3},$$

in which V is the volume, would express r. We would then expect that U_e could be calculated by

$$U_e = -N\frac{\epsilon^2}{D}\left(\frac{2N}{V}\right)^{1/3},$$

and this in fact is the equation employed by Ghosh. This equation might be valid for the electrical energy of a salt crystal, but would not be valid for uniunivalent electrolytes. In the latter case, the ions possess a motion due to thermal agitation, and the problem is resolved into finding the number of positive and negative ions in the same volume element. This important consideration marks the departure of Debye and Hückel's theory from that of Ghosh.

Debye and Hückel now obtain a general equation for the electrical potential of the solution by means of Poisson's and Boltzmann's equations. Let

$$N_1 \cdots N_i \cdots N_s$$

be the number,

$$z_1 \cdots z_i \cdots z_s$$

[1] $G = -\frac{A}{T}$ and $\Phi = -\frac{F}{T}$ which is Planck's thermodynamic potential.

the valences of the ions designated,

$$n_1 \cdots n_i \cdots n_s$$

the number of each species per cubic centimeter, and

$$\nu_1 \cdots \nu_i \cdots \nu_s$$

the number of ions of the ith kind formed by the dissociation of one molecule of electrolyte. According to Poisson's equation, the potential, ψ, in a field of electrification of density ρ must be

$$\nabla \cdot \nabla\psi = -\frac{4\pi}{D}\rho, \tag{v}$$

where ∇ is the operator "nabla." Further, according to Boltzmann's law, the number of ions of the ith kind in an element of volume dV is

$$n_i e^{-z_i(\epsilon\psi/kT)}dV,$$

their density

$$n_i e^{-z_i(\epsilon\psi/kT)},$$

and, consequently,

$$\rho = \epsilon\Sigma n_i z_i e^{-z_i(\epsilon\psi/kT)}, \tag{vi}$$

where ϵ is the electronic charge, k is the Boltzmann constant, and e the base of the natural logarithms. Eliminating ρ from (v) and (vi), we obtain

$$\nabla \cdot \nabla\psi = -\frac{4\pi\epsilon}{D}\Sigma n_i z_i e^{-z_i(\epsilon\psi/kT)} = -\frac{4\pi e\Sigma n_i z_i}{D}\sinh\frac{z_i\epsilon\psi}{kT},$$

which without appreciable error may be reduced to

$$\nabla \cdot \nabla\psi = \frac{4\pi\epsilon^2}{DkT}\Sigma n_i z_i^2\psi. \tag{vii}$$

Now let

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT}\Sigma n_i z_i^2 \tag{viii}$$

and, therefore, (vii) may be written

$$\nabla \cdot \nabla\psi = \kappa^2\psi. \tag{ix}$$

κ is a very important quantity in this theory, and possesses the dimensions of a reciprocal length. $1/\kappa$ has numerical values from 10^{-7} to 10^{-8} cms. or molecular dimensions at moderate concentrations of the electrolyte.

The primitive of equation (ix) gives the total potential which, for the case of a uniunivalent electrolyte, becomes

$$\psi = \frac{\epsilon}{D}\frac{e^{-\kappa r}}{r} = \frac{\epsilon}{D}\frac{1}{r} - \frac{\epsilon}{D}\frac{1 - e^{-\kappa r}}{r}.$$

It is important to note that ϵ/Dr is the potential of an ion in a medium of dielectric constant, D, when it is not influenced by other ions. The desired potential is the second member on the right of this equation which represents the potential of an ion when influenced by other ions. For small values of r, $(1 - e^{-\kappa r})/r = \kappa$, and the potential equals $-(\epsilon/D)\kappa$. Thus $1/\kappa$ in Debye and Hückel's theory functions in a manner similar to the mean distance r in other theories.

Since $1/\kappa$ has molecular dimensions at higher concentrations, it becomes necessary to introduce considerations which depend on the dimensions of the ions. "a" is a length which is the mean value of the distance which a positive or negative ion can approach another ion, and will be of the order of magnitude of an ionic diameter. This distance will be greater than the distance between the atoms of a crystal because of the probable formation of water of hydration on the ions.

Introducing this latter consideration, it is found that the potential energy, U_e, for the general case is given by

$$U_e = -\sum \frac{N_i z_i^2}{2} \frac{\epsilon^2 \kappa}{D} \frac{1}{1 + \kappa a_i} . \tag{x}$$

Substituting this value for U_e in equation (iii) and performing the integration, it is found that

$$\Phi_e = \sum N_i \frac{z_i^2 \epsilon^2}{DT} \frac{\kappa}{3} \chi_i, \tag{xi}$$

where

$$\chi_i = 1 - \tfrac{3}{4}(\kappa a_i) + \tfrac{3}{5}(\kappa a_i)^2 - \cdots \tag{xii}$$

and, therefore, from (iv) and (xi)

$$\Phi = \sum_0^s N_i(\phi_i - k \log c_i) + \sum_1^s N_i \frac{z_i^2 \epsilon^2}{3D} \frac{\kappa}{T} \chi_i. \tag{xiii}$$

From this value of Φ, it is purely a matter of mathematics and simple thermodynamics to deduce the laws of the freezing-point lowering and the equation for the osmotic coefficient. The general equation for the osmotic coefficient is

$$1 - \varphi = w \frac{\epsilon^2}{6DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} n \Sigma \nu_i} \frac{\Sigma \nu_i z_i^2 \sigma_i}{\Sigma \nu_i z_i^2} \tag{xiv}$$

where w is the valence factor previously mentioned, or

$$w = \left(\frac{\Sigma \nu_i z_i^2}{\Sigma \nu_i} \right)^{3/2},$$

σ_i is given by the series

$$\sigma_i = 1 - \tfrac{3}{2}(\kappa a_i) + \tfrac{9}{5}(\kappa a_i)^2 - 2(\kappa a_i)^3 + \cdots, \tag{xv}$$

$n = \Sigma n_i$, and $\nu = \Sigma \nu_i$. In very dilute solutions, (xiv) reduces to

$$1 - \varphi = w \frac{\epsilon^2}{6DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} n\Sigma\nu_i}. \qquad \text{(xvi)}$$

In this equation, ϵ equals 4.77×10^{-10} electrostatic units; D equals 88.23 when T equals 273; and k equals 1.346×10^{-16} ergs. Since n is the number of ions in a cubic centimeter, it equals $6.06 \times 10^{20}c$, where c is the molal concentration. Upon substituting these values in equation (xvi), we obtain

$$1 - \varphi = 0.270w\sqrt{\nu c} \qquad \text{(xvii)}$$

at 0° C. In order to derive the equation for the activity coefficient, we first obtain from equation (95), upon neglecting the linear term, the equation for the van't Hoff factor, $[i]$. This equation which is valid in the very dilute solutions is

$$[i] = \nu - \frac{2.303\nu\beta\alpha'}{\alpha' + 1} c^{\alpha'}.$$

Since $\varphi = i/\nu$, and $\alpha' = 0.5$, we find that

$$3(1 - \varphi) = 2.303\beta c^{0.5} = - ln\ \gamma \qquad \text{(xviii)}^1$$

since $\log \gamma = - \beta c^{0.5}$. From (xvii) and (xviii), we obtain

$$\left.\begin{aligned} ln\ \gamma &= - 0.81w\sqrt{\nu c} \\ \text{or} \qquad \log \gamma &= - 0.351w\sqrt{\nu c}. \end{aligned}\right\} \qquad \text{(xix)}$$

From these last equations, the two most important results of the Debye and Hückel theory may be readily derived. In the first place $(1 - \varphi)$ and $\log \gamma$ are proportional at high dilutions to $\sqrt{c}$ at constant pressure and temperature. Secondly, the valence factor, w, appears, which differs according to the valence type of electrolyte. For uniunivalent, biunivalent, bibivalent, triunivalent, and tribivalent electrolytes, w equals 1, 2.83, 8, 5.2, and 16.6, respectively.

In the more concentrated solutions, according to (xiv), we must introduce σ_i which is given by the linear equation (xv) and which is a function of κ, and the mean apparent ionic diameter, a. Since, by equation (viii), κ is proportional to $(\Sigma n_i)^{1/2}$ and therefore to $c^{1/2}$, σ_i is given by a linear equation in powers of c, ascending by the exponent $\frac{1}{2}$. From equations (xiv) and (xv), we may obtain

$$\log \gamma = - 0.351w\sqrt{\nu c} + \alpha_2(\nu c) - \beta_2(\nu c)^{3/2} + \gamma_2(\nu c)^2 - \cdots, \qquad \text{(xx)}$$

where α_2, β_2, etc., are constants. The second member on the right of this equation is in agreement with the linear term in the approximation equation (85), employed throughout the thermodynamic discussion. Indeed, from

[1] Brönsted, *J. Am. Chem. Soc.*, **43**, 763 (1920); Brönsted and La Mer, *J. Am. Chem. Soc.*, **46**, 555 (1924).

equation (xx), it can be seen how equation (85) could be modified to meet the demands of theory and to attain greater accuracy.

To verify equation (xvii), Debye and Hückel employed all the available freezing-point data, and found that as the concentration approached zero, these data appeared generally to approach the values required by the theory. These results, however, cannot be said to establish their limiting law. As previously shown, the freezing-point data in the very dilute solutions are indeed too fragmentary for this purpose. More recently, very important evidence for Debye and Hückel's theory has been obtained by Brönsted and La Mer.[1] They measured with great accuracy the solubility of a number of very slightly soluble higher order cobalt compounds in salt solutions of various valence types. The results obtained agree very strikingly with the square root concentration law and seem to verify the correctness of the valence factor, w.

This important theory, complicated because of the very thorough mathematical treatment, is based on very simple assumptions, which are, firstly, complete dissociation, and, secondly, that the departure of electrolytes from the law of ideal solutes in very dilute solutions is caused solely by the electrical field effect, and not to any chemical reactions between the ions. Cases of ionic interaction are not covered. One consequence of this theory, in the concentrated solutions and in cases of simple ions where no reactions take place between the ions, is that marked additivity relationships should be observed among the partial free energies. That this is probably the case for the simplest ions will be shown later when we come to consider the direct determination of the activity coefficients of the individual ions. Any evidence of this kind is indeed strong support for the theory of complete dissociation.

The Activity Coefficients of Electrolytes in Mixtures

The activity coefficient of an ion of an electrolyte has been defined as the ratio of its activity to the molal concentration of the ion. In a 0.1 molal solution of sulphuric acid, the activity coefficient of the hydrogen ion equals $\frac{a_+}{0.2}$, and of the sulphate ion $\frac{a_-}{0.1}$. This we shall call, after the nomenclature of Brönsted,[2] the stoichiometrical activity coefficient. The activity coefficient of an ion in a solution containing other electrolytes may according to this usage be defined by the ratio of its activity to its stoichiometrical concentration. The activity coefficient of a uniunivalent electrolyte will then be equal to the square root of the product of the activity coefficients of the ions. In general, if an electrolyte dissociates into ν^+ cations and ν^- anions, its activity coefficient in the mixture, γ, will be equal to $(\gamma_+^{\nu^+}\gamma_-^{\nu^-})^{1/\nu}$, where γ_+ and γ_- are the activity coefficients of the ions. According to this definition, the activity coefficient of 0.1 molal

[1] *J. Am. Chem. Soc.*, **46**, 555 (1924). See also Noyes, *ibid.*, **46**, 1098 (1924).

[2] *J. Am. Chem. Soc.*, **42**, 761 (1920); Kgl. Danske Videnskab. Selskab. Math.-fys. Medd. **II**, 10 (1919).

hydrochloric acid in a 0.5 molal strontium chloride solution will equal $\left(\frac{a_H \; a_{Cl}}{0.1 \; 1.1}\right)^{1/2}$; the activity coefficient of 0.1 molal hydrochloric acid in a molal sodium sulphate solution will equal $\left(\frac{a_H \; a_{Cl}}{0.1 \; 0.1}\right)^{1/2}$; while the activity coefficient of the 0.5 molal strontium chloride in the above solution containing 0.1 molal hydrochloric acid will be $\left(\frac{a_{Sr} \; a_{Cl}^2}{0.5 \; (1.1)^2}\right)^{1/3}$.

The activity coefficient of one electrolyte in the presence of another may be computed either from measurements of electromotive forces of suitable cells, or by measuring the solubility of a salt in salt solutions. The electromotive force method, if not complicated by secondary reactions, permits the determination of the activity coefficient of an electrolyte at all available concentrations in the presence of another electrolyte at all available concentrations. On the other hand, the measurement of the solubility of one electrolyte in a solution of another is always limited to the saturated solution of one of the electrolytes. The electromotive force method, although more general, is not applicable to the study of all mixtures, because of the fact that suitable cells are not always available. For example, it is possible to determine by a direct method the activity coefficient of hydrochloric acid in solutions of chlorides by means of cells of the type

$$H_2 \,|\, HCl\ (c_1),\ KCl\ (c) \,|\, AgCl \,|\, Ag,$$

but, owing to secondary effects, the activity coefficient of sodium chloride in solutions of potassium chloride cannot be directly determined by the cell

$$\begin{matrix} Na_x \\ Hg \end{matrix} \Big| \, NaCl\ (c_1),\ KCl\ (c) \, \Big| \, AgCl \,|\, Ag.^1$$

The Activity Coefficient of Hydrochloric Acid in Solutions of Chlorides: It has already been shown (Table VIII) that by measuring cells of the type

$$H_2 \,|\, HCl\ (c_1) \,|\, HgCl \,|\, Hg$$

and

$$H_2 \,|\, HCl\ (c_1),\ MeCl_x\ (c) \,|\, HgCl \,|\, Hg,^2$$

the free energy decrease attending the reaction

$$HCl\ (c_1).[MeCl_x\ (c)] = HCl\ (c_1)$$

may be computed. This decrease in free energy is equal to the difference in partial molal free energies of the acid in pure acid solution and the salt solution, and, therefore, according to equation (49)

$$(-\Delta\overline{F}) = -(\overline{F}_2 - \overline{F}_{2(s)}) = RT ln \frac{a_{H(s)} a_{Cl(c+c_1)}}{a_{H(c_1)} a_{Cl(c_1)}}, \qquad (49)$$

[1] Unpublished measurements—Harned.

[2] Silver-silver chloride electrodes may also be employed, and, in fact, are much more reliable in dilute solutions.

where $a_{H(s)}$ is the activity of the hydrogen ion in the salt solution. Consequently, if the activity product, $a_{H(c_1)}a_{Cl(c_1)}$, of the pure acid at a concentration c_1 is known, the activity product of the hydrogen and chloride ions in the mixed solutions may be calculated. The activity coefficient of the hydrochloric acid in the solution may readily be calculated from the activity product of the ions according to

$$\gamma = \sqrt{\frac{a_{H(s)}a_{Cl(c+c_1)}}{c_1(c+c_1)}}.$$

Measurements of these cells, principally, at 25° C., containing varying salt and constant acid concentrations, and containing both varying salt and acid concentrations at constant total concentration have been made by a number of investigators.[1] From the data of Harned, and Harned and Brumbaugh, the activity coefficients of 0.1 molal hydrochloric acid in solutions of varying quantities of uniunivalent and unibivalent chlorides and of 0.01 and 0.001 molal hydrochloric acid in solutions of potassium chloride have been computed. These values are given in Table XIX. The activity coefficients of the acid at 0.1, 0.01, and 0.001 molal concentrations have been taken to be 0.824, 0.924, and 0.971, respectively (Table XII). The second column contains the activity coefficients of pure hydrochloric acid. The activity coefficients of the acid in the different salt solutions are denoted γ (KCl), γ (NaCl), etc.

The Ionic Strength: In Fig. 9, the activity coefficient of 0.1 molal hydrochloric acid in potassium chloride solutions has been plotted against the total molal concentration (curve No. 1), and also the activity coefficient of 0.1 molal acid in calcium chloride solutions against both the total molal (curve No. 2) and weight equivalent (curve No. 3) concentrations. There is a wide departure from uniformity between these curves. This is caused in part, at least, by

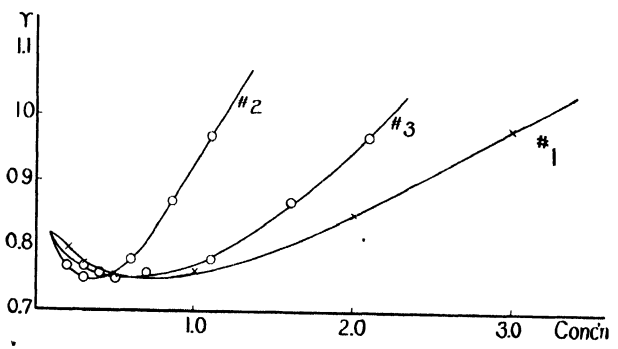


FIG. 9. Concentration Plot of Activity Coefficients of Hydrochloric Acid in Halide Solutions

[1] Harned, *J. Am. Chem. Soc.*, **38**, 1986 (1916); **42**, 1808 (1920). Loomis, Essex and Meacham, *J. Am. Chem. Soc.*, **39**, 1133 (1917). Ming Chow, *J. Am. Chem. Soc.*, **42**, 497 (1920). Harned and Brumbaugh, *J. Am. Chem. Soc.*, **44**, 2729 (1922).

TABLE XIX

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN UNIUNIVALENT AND UNIBIVALENT CHLORIDE SOLUTIONS AT 25°

0.1 molal HCl					0.01 molal HCl		0.001 molal HCl		0.1 molal HCl				
$(c + c_1) = \mu$	γ (Pure HCl)	γ (KCl)	γ (NaCl)	γ (LiCl)	$(c + c_1) = \mu$	γ (KCl)	$(c + c_1) = \mu$	γ (a) (KCl)	$(c + c_1)$	μ	γ ($BaCl_2$)	γ ($SrCl_2$)	γ ($CaCl_2$)
0.1	0.824	0.824	0.824	0.824	0.01	0.924	0.001	0.971	0.1	0.1	0.824	0.824	0.824
0.2	0.795	0.795	0.797	0.798	0.06	0.839	0.051	0.861	0.2	0.4	0.748	0.760	0.766
0.3	0.781	0.772	0 774	0.782	0 11	0.808	0.101	0.813	0.3	0.7	0.738	0.743	0.748
0.5	0.775	0.754	0.763	0.794	0 31	0.761	0.301	0.774	0.4	1	0.735	0.743	0.757
1	0.817	0.760	0 788	0.846	0.51	0.733	0.501		0.6	1.6	0.759	0.772	0.778
2	1.016	0.847	0.950	1.093	1.01	0.739	1.001	0.756	0 85	2.35	0.820	0 846	0.866
3	1.343	0.978	1.195	1.489	2.01	0.800	2.001		1.1	3.1	0.898	0.931	0.967
4	1.831	1.154	1.496	2.069	3.01	0.915	3.001	0 973	1.4	4	1.016	—	—

(a) The values of γ for 0 001 M acid in 0.3, 1, and 3 M potassium chloride are taken from more recent and more exact measurements than those given by Harned and Brumbaugh.

the fact that the concentrations have been expressed in units which do not eliminate the change in properties of the solution when a unibivalent chloride is substituted for a uniunivalent chloride. For the purposes of calculation, it would be a great convenience to eliminate any differences caused by a difference in electrostatic field intensity in going from the uniunivalent to a unibivalent solution. One way by means of which this may be done is by expressing the concentration in a unit such that, at equal values of this unit, all electrolytes are subject to the same electrostatic forces. Lewis and Randall have suggested for this purpose a unit which they have called the "ionic strength" and denoted μ. To obtain a value for this unit of an electrolyte or a mixture of electrolytes, multiply the stoichiometrical concentration of the ion by the square of its valence. Add up these quantities for all the ions in the solution and divide by two. The result will be the ionic strength. As an example, consider a mixture of 0.1 molal hydrochloric acid in 1 molal barium chloride. μ will equal $\frac{[0.1 + 2.1 + 4]}{2}$, or 3.1. When the added salt is uniunivalent, μ is equal to the total concentration. The values of μ for the acid salt mixtures are given in Table XIX.

If, now, the activities of the 0.1 molal acid in the salt solutions be plotted against μ, as shown in Fig. 10, the curves are all uniform and approach the

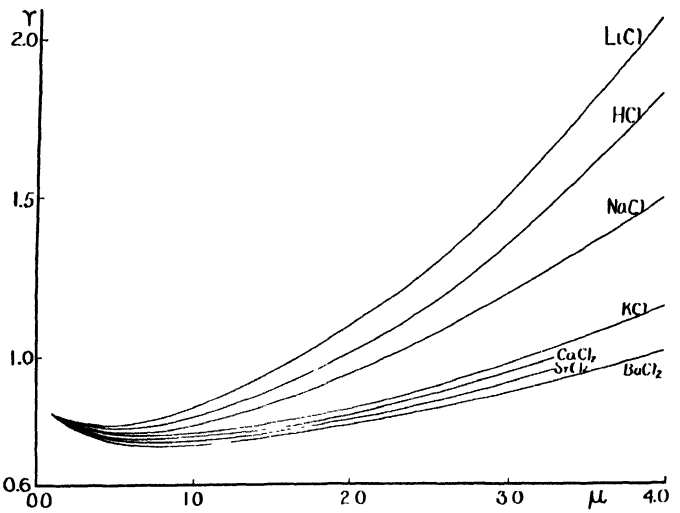


FIG. 10. Ionic Strength Plot of Activity Coefficients of Hydrochloric Acid in Halide Solutions

0.1 molal value uniformly. It is important to note that each of these curves has a minimum, and possesses a form similar to a similarly drawn curve for pure hydrochloric acid. Further, the activity coefficient of the acid is greater in solutions of the electrolytes which have the higher hydration values, or which, when alone in aqueous solutions, have the higher activity coefficients.

In the more dilute solutions, the activity coefficient of the acid in the salt solutions nearly equals that in the pure acid solution of the same ionic strength, which point is well illustrated by Table XIX. These considerations led Lewis and Randall[1] to the empirical rule that "in dilute solutions, the activity coefficient of a given electrolyte is the same in all solutions of the same ionic strength." That this rule is approximately true in the dilute solutions may be seen from the similar plots of the activity coefficients of 0.01, and 0.1 molal hydrochloric acid in potassium chloride solutions shown in Fig. 11. This

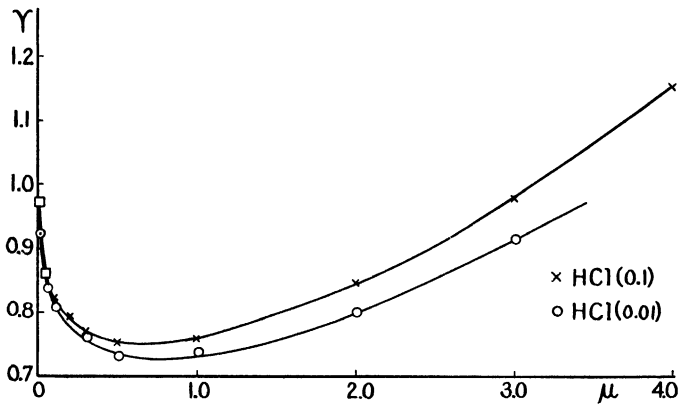


FIG. 11. Activity Coefficient of Hydrochloric Acid of Different Strengths in Potassium Chloride Solutions

rule is to be taken as an approximation, only within the error of experiment in very dilute solutions, since these curves exhibit a pronounced difference of curvature in the more concentrated solutions, and it is not likely that they become identical in the dilute solutions.[2]

The activity coefficients of the acid in 0.001 molal hydrochloric acid containing potassium chloride are in all cases higher at the same ionic strength than those in the 0.01 molal solutions. According to these results, it is clear that, at constant total molality, the activity coefficient of the acid will pass through a minimum.

An Approximate Calculation of the Activity Coefficients of Hydrochloric Acid in the Uniunivalent Chloride Solutions: It was found that the activity coefficient of an electrolyte in aqueous solution and at constant temperature and pressure could be computed by an empirical equation, which was

$$\log \gamma = \alpha c - \beta c^{\alpha'}. \tag{85}$$

It is a matter of considerable interest to find out whether this equation may be adapted for the calculation of the activity coefficient of one electrolyte in

[1] *J. Am. Chem. Soc.*, **43**, 1112 (1921).

[2] Brönsted, *J. Am. Chem. Soc.*, **44**, 877 (1922). Lewis and Randall, Thermodynamics, McGraw-Hill Co., pp. 363–369.

the presence of another electrolyte. An attempt in this direction was made by Harned and Brumbaugh, and, although their calculation is admittedly approximate, it serves to illustrate the complicated behavior of mixtures. Equation (85) when adapted for the mixtures is

$$\log \gamma = \alpha c_1 - \beta \mu^{\alpha'} + \alpha''(\mu - c_1), \qquad (105)$$

where α, β and α' are the constants used in computing the activity coefficients of the pure acid, and α'' is another constant which functions in the equation for the mixtures in a manner similar to α in equation (85).

In Table XX, the values of γ of the acid in the uniunivalent chloride mixtures, computed by means of equation (105), are compared with the observed values taken from Table XIX. α, β, α' are the same as those previously employed in calculating the activity coefficients of pure hydrochloric acid. The α'' values employed for each mixture are also included in the table.

TABLE XX

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SALT SOLUTIONS

$\alpha = 0.20$; $\beta = 0.288$; $\alpha' = 0.450$

0.1 MHCl							(0.01 MHCl)		
μ	γ (KCl) ($\alpha'' = 0.150$)		γ (NaCl) ($\alpha'' = 0.178$)		γ (LiCl) ($\alpha'' = 0.215$)		μ	γ (KCl) ($\alpha'' = 0.150$)	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)		(Obs.)	(Calc.)
0.1	0.824	0.827	0.824	0.827	0.824	0.827	0.01	0.924	0.924
0.2	0.795	0.786	0.797	0.791	0.799	0.798	0.06	0.839	0.848
0.3	0.772	0.763	0.774	0.774	0.782	0.786	0.11	0.808	0.813
0.5	0.754	0.750	0.763	0.759	0.794	0.786	0.31	0.761	0.753
1	0.760	0.740	0.788	0.780	0.846	0.842	0.51	0.733	0.732
2	0.847	0.816	0.950	0.922	1.093	1.084	1.01	0.739	0.729
3	0.978	0.962	1.195	1.159	1.489	1.484	2.01	0.800	0.809
4	1.154	1.169	1.496	1.502	2.069	2.095	3.01	0.915	(0.951)

The agreement between the observed and calculated values is good, particularly in the case of the lithium chloride solutions. The values of γ of the acid in potassium chloride solutions at both 0.01 and 0.1 molal may be calculated with a fair degree of accuracy by employing the same constants. That the problem is very complicated, however, becomes evident when it is necessary to employ a fourth constant, α'', which differs considerably from the value of α for the individual salt, and seems to have no simple relation to it. Further, another effect appears when the acid is very dilute and the salt-acid ratio is very high, which makes equation (105) useless for calculations in solutions containing very dilute acid.

This phenomenon can best be considered by observing the variation of the activity coefficient of the acid in solutions of constant total molality. Loomis, Essex and Meacham found that, in solutions of 0.1 total molality containing potassium chloride, the activity coefficient of hydrochloric acid was somewhat greater in solutions which contained the larger

quantity of hydrochloric acid. They extended their results only to solutions as dilute as 0.01 molal acid strength. Ming Chow, from measurements of a hydrogen-calomel cell, found no deviation greater than 1.3 per cent in solutions of 0.1 molal total strength. In Table XXI are given the values computed from the results of Ming Chow at 0.1 molal total concentration, and from the results of Harned and Brumbaugh at 3, 1, and 0.1 molal total concentrations.

TABLE XXI

ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN SOLUTIONS OF POTASSIUM CHLORIDE AT CONSTANT TOTAL MOLALITY

c_1 (Acid)	γ (Total 3M)	γ (Total 1M)	γ (Total 0.1M) (Ming Chow)	γ (Total 0.1M)
3	1.343	—	—	—
1	1.175	0.816	—	—
0.1	0.973	0.759	0.824	0.824
0.01	0.915	0.739	0.818	0.808
0.001	0.973	0.756	0.825	0.814

From these results, it would seem that the value of γ has a minimum in the neighborhood of 0.01 molal acid concentration, although at 0.1 molal total concentration it is barely noticeable. This behavior was thought by Harned and Brumbaugh to indicate that in those mixtures of dilute acid in which the salt to acid ratio is high, there is an effect on the activity coefficient which is a function of this ratio.

The Activity Coefficients of Salts in Salt Solutions from Solubility Data: We have found as a general principle that, when a system of more than one phase at constant pressure and temperature is in equilibrium with another phase, the activity of any component is the same in each phase. If, then, we have a salt in equilibrium with its saturated solution, the activity of the solid equals the activity of the salt in the saturated solution. At constant pressure and temperature, the activity of the solid will be a constant, k. Consequently, under these conditions for a uniunivalent electrolyte,

$$k = a_2 = a_+a_-, \tag{106}$$

where a_2 is the activity coefficient of the salt in the solution, which by definition equals the activity product of its ions. From this equation we find that

$$k = \gamma_+c_+\gamma_-c_- = \gamma_+\gamma_-c_+c_-, \tag{107}$$

in all solvents, where c_+ and c_- are the stoichiometrical concentrations of the ions. It will be found convenient to divide solutions of mixed electrolytes into two classes; solutions containing electrolytes which have no ion in common which we term hetero-ionic, and solutions of electrolytes possessing a common ion which we denote homo-ionic, according to the usage of Brönsted.[1] In a

[1] *J. Am. Chem. Soc.*, **42**, 761 (1920).

hetero-ionic solvent,

$$c_+ = c_- = S,$$

where S is the solubility, and, therefore,

$$\gamma = (\gamma_+\gamma_-)^{1/2} \propto \frac{1}{S}. \tag{108}$$

In a homo-ionic solvent, either c_+ or c_- may equal S, and the other ion concentration equal the sum of its stoichiometrical concentration for both electrolytes. If the anion is common to both electrolytes,

$$k = \gamma_+\gamma_- Sc_-$$

and

$$\gamma \propto \left(\frac{1}{Sc_-}\right)^{1/2}. \tag{109}$$

In a similar manner if the cation is common to both electrolytes,

$$\gamma \propto \left(\frac{1}{Sc_+}\right)^{1/2}. \tag{109}$$

By means of equations (108) and (109) it is possible to determine the activity coefficient of a salt in a mixture if the activity coefficient of the pure salt in its saturated solution is known. If this is not known, it is then possible, if sufficient experimental data are available, to extrapolate graphically by plotting $\frac{1}{S}$, or $\left(\frac{1}{Sc_-}\right)^{1/2}$, or $\left(\frac{1}{Sc_+}\right)^{1/2}$ against some root of the concentration or the ionic strength. For, when μ equals zero, γ equals 1, and $\frac{1}{S}$, $\left(\frac{1}{Sc_-}\right)^{1/2}$, or $\left(\frac{1}{Sc_+}\right)^{1/2}$ will equal the reciprocal of the proportionality factor.

The most complete series of measurements of a simple sparingly soluble salt in salt solutions was carried out by Bray and Winninghoff [1] on the solubility of thallous chloride. Lewis and Randall [2] have extrapolated their data by the method mentioned above and obtained $\frac{1}{70.3}$ for the factor of proportionality. If we let $c_\pm$ equal the square root of the product of the stoichiometrical concentrations of the thallous and chloride ions, γ will equal $\frac{1}{70.3 \times c_\pm}$ in all of the salt solutions. By this means, the activity coefficients of thallous chloride have been calculated directly from Bray and Winninghoff's results and compiled in Table XXII. The concentrations are expressed in equivalents per liter. No correction has been employed to convert them to the 1000 g. scale.

[1] *J. Am. Chem. Soc.*, **33**, 1663 (1911).
[2] *J. Am. Chem. Soc.*, **43**, 1112 (1921).

TABLE XXII

ACTIVITY COEFFICIENTS OF THALLOUS CHLORIDE IN SALT SOLUTIONS AT 25° C.

c (Equivalents per Liter of Added Salt)	γ						
	KNO_3	KCl	HCl	$TlNO_3$	$BaCl_2$	Tl_2SO_4	K_2SO_4
0	0.885	0.885	0.885	0.885	0.885	0.885	0.885
0.02	0.829	(0.843)	(0.844)	(0.836)	(0.829)	0.803	0.800
0.025	(0.819)	0.831	0.833	0.825	0.814	(0.789)	(0.787)
0.05	0.779	0.784	0.788	0.759	0.763	0.726	0.733
0.1	0.725	0.701	0.713	0.678	0.683	0.643	0.666
0.2	(0.655)	0.610	0.628	—	0.595	—	(0.588)
0.3	0.615	—	—	—	—	—	0.547
1	0.463	—	—	—	—	—	0.417

(The values in parentheses were obtained by graphical interpolation.)

In Fig. 12, the activity coefficients of thallous chloride in the different salt solutions are plotted against the ionic strength. The curves at the higher dilutions approach the value of pure thallous chloride in a similar manner. No such uniformity would have been observable if the values had been plotted against the equivalent concentrations. This is a further illustration of the value of employing the ionic strength, or some similar quantity in studying the behaviors of mixtures. It appears that all of these curves obey an equation of the same form.

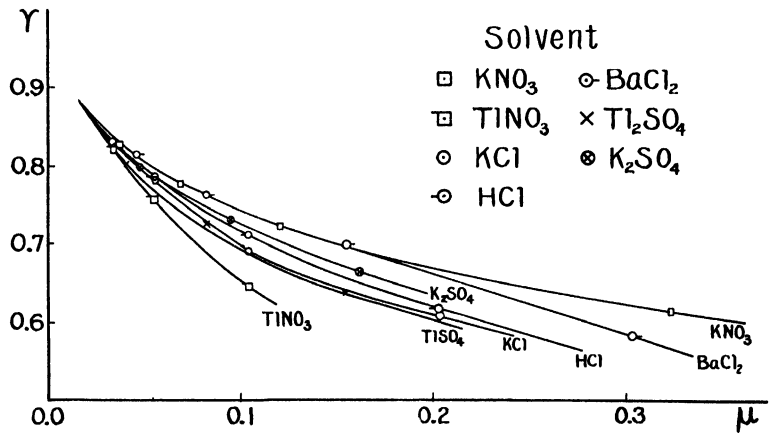


FIG. 12. Activity Coefficients of Thallous Chloride in Salt Solutions

The curves show that the influence of one electrolyte on the activity coefficient of another is a problem of great complexity. Each mixture exhibits individual behavior even in solutions of ionic strength as low as 0.03. In fact, Brönsted [1] has pointed out many

[1] *J. Am. Chem. Soc.*, 44, 877 (1922).

examples of salt mixtures which exhibit even greater individual effects than those just considered.

We shall conclude the present discussion by reference to some of the important recent contributions to the study of the solubility of salts in salt solutions. The classic investigations on this subject begun by A. A. Noyes,[1] and followed by the papers of Noyes and Bray,[2] Bray and Winninghoff,[3] Harkins and Winninghoff,[4] Harkins and Paine,[5] and Harkins and Pearce [6] have been exhaustively discussed by Lewis and Randall.[7] Important contributions to this subject have been recently made by Brönsted.[8] In the first of Brönsted's papers, it was shown that the general nature of the solubility of salts in both hetero- and homo-ionic solutions could be predicted in dilute solutions from considerations involving the activity function and the variation of the activity function with the concentration in the mixtures. Brönsted and Petersen studied the solubility of many compounds of a higher order in salt solutions, and found many and varied specific behaviors. In the last of the articles, entitled "The Principle of the Specific Interaction of Ions," the specific behaviors have been considered on theoretical grounds. These investigations have added much to our knowledge of the thermodynamics of salt mixtures.

The Mass Action Law and the Inner Equilibrium of Solutions of Electrolytes. Bjerrum's Theory of Ionic Hydration

The preceding discussion, with the exception of what has been said concerning the significance of the different coefficients and the conductance ratio, rests on thermodynamic reasoning and to this extent is exact. Although it is impossible by pure thermodynamics alone to prove what molecular and ionic species are present in a solution and how these interact, it is possible by the introduction of assumptions outside the domain of thermodynamics to account for certain observed behaviors. We may cite, for example, the theory of van der Waals, which, within certain limits, accounts satisfactorily for the Joule-Thomson effect, and other behaviors of gases at high pressures. When we come to consider such complicated systems as solutions, some partially successful hypotheses regarding the equilibria between ions and molecules have been proposed. Although these give a somewhat vague picture of what must be the true condition of a solution of an electrolyte, their importance as a hint toward the solution of this most difficult problem cannot be overestimated.

If the conductance ratio be taken as a measurement of the true degree of dissociation, then, upon applying the law of mass action to the dissociation of a uniunivalent electrolyte, we obtain the well-known Ostwald dilution law:

$$K = \frac{\left(\frac{\Lambda}{\Lambda_0}\right)^2 c}{\left(1 - \frac{\Lambda}{\Lambda_0}\right)},$$

[1] *Z. physik. Chem.* (1890).
[2] *J. Am. Chem. Soc.*, **30**, 1643 (1908).
[3] *J. Am. Chem. Soc.*, **33**, 1663 (1911).
[4] *J. Am. Chem. Soc.*, **33**, 1827 (1911).
[5] *J. Am. Chem. Soc.*, **41**, 1155 (1919).
[6] *J. Am. Chem. Soc.*, **38**, 2679 (1916).
[7] *J. Am. Chem. Soc.*, **43**, 1112 (1921).
[8] *J. Am. Chem. Soc.*, **42**, 761 (1920); Brönsted and Petersen, *J. Am. Chem. Soc.*, **43**, 2265 (1921); Brönsted, *J. Am. Chem. Soc.*, **44**, 877 (1922).

where K is the dissociation constant of the electrolyte. This equation is valid for solutions of many weak electrolytes. For instance, Kendall [1] has shown that it is valid for solutions of acetic acid from 0.0005 to 0.07 normal. Above this latter concentration there is a departure from the law. Strong electrolytes in aqueous solutions show no agreement with the Ostwald dilution law except possibly in extremely dilute solutions.[2] The dissociation of strong electrolytes in non-aqueous solvents appears to conform with the law in dilute solutions.[3] This law has therefore been regarded as a limiting law for solutions of all types of electrolytes in all solvents.

As against this point of view, many investigators consider the difference between the behavior of strong and weak electrolytes as a difference of kind and not of degree, and have regarded strong electrolytes to be completely dissociated. But this point of view has not thrown any further light on the inner equilibria which very probably exist between the ions and molecular species, for example, the solvent molecules in solutions.

If we assume that the dissociation of a uniunivalent electrolyte is represented by

$$CA \rightleftharpoons C^+ + A^-,$$

we have shown that according to the general law of equilibrium the dissociation constant, K, will be given by

$$K = \frac{a_+ a_-}{a_2}.$$

Owing to our lack of knowledge of the concentration of the undissociated molecule, the convention was adopted that K equals unity, and, therefore,

$$a_2 = a_+ a_-.$$

All values of activity products and activity coefficients of electrolytes previously recorded are in accord with this convention.

Let us now assume that the equilibria of a solution of a strong electrolyte are represented by the following reactions:

$$(a) \quad CA \rightleftharpoons C^+ + A^-,$$
$$(b) \quad C^+ + hH_2O \rightleftharpoons C^+.hH_2O,$$
$$(c) \quad A^- + jH_2O \rightleftharpoons A^-.jH_2O,$$

where $C^+.hH_2O$ and $A^-.jH_2O$ are the ion hydrates. If we let a_w, a_h, a_j equal the activities of the water molecule, and the two ion hydrates, respectively, we obtain for the equilibrium constant of all three reactions

$$K = \frac{a_h a_j}{a_2 a_w^{(h+j)}}, \tag{110}$$

[1] *Med. Veten. Akad. Nobelinstitut*, **2**, No. 38 (1913).

[2] Weiland, *J. Am. Chem. Soc.*, **40**, 131 (1918).

[3] Kraus, Properties of Electrically Conducting Systems, Chaps. III and IV, Chemical Catalog Co.

or

$$K = \frac{a_h a_j}{a_+ a_- a_w^{(h+j)}}, \tag{111}$$

since a_2 equals a constant times a_+a_-. Equation (111) could have been obtained from the chemical equations (*b*) and (*c*) which would represent the equilibria on the theory of complete dissociation. If, as before, we adopt the convention that K equals unity, we obtain for the activity of the electrolyte or the activity product of the ions of the electrolyte

$$a_2 = a_+a_- = \frac{a_h a_j}{a_w^{(h+j)}}. \tag{112}$$

This equation has been employed by Bjerrum [1] for the purpose of computing ionic hydration values from activity data in concentrated solutions. Bjerrum's theory is based on the assumption of complete dissociation, and the assumption that the electromotive force method measures the activities of the non-hydrated ions. The above deduction is more general than Bjerrum's, since equation (112) will be valid on either the theory of complete or incomplete dissociation, providing that the chemical equations (*b*) and (*c*) or (*a*), (*b*) and (*c*) represent the equilibria in the solution.

Taking the logarithm of equation (112), we obtain

$$\log a_+a_- = \log a_h a_j - (h + j) \log a_w. \tag{113}$$

Substituting the activity coefficients,

$$\log \gamma c = \log \gamma' c - \frac{(h + j)}{2} \log a_w \tag{114}$$

is obtained, where γ' is the square root of the activity coefficient product of the hydrated ions. Since $a_w = \frac{p}{p_0}$, we find that

$$\log \gamma = \log \gamma' - \frac{(h + j)}{2} \log \frac{p}{p_0}. \tag{115}$$

According to equation (97),

$$\log \frac{p_0}{p} = \frac{c}{55.5} [i] \tag{97}$$

and equation (115) becomes

$$\log \gamma = \log \gamma' + \left(\frac{h + j}{2} \right) \frac{c}{55.5} [i]. \tag{116}$$

According to equation (116), the second member on the right becomes negligible in dilute solutions, and γ and γ' become identical. Therefore, in dilute solutions,

$$\log \gamma = \log \gamma' = - \beta c^{\alpha'}. \tag{117}$$

[1] *Z. anorg. Chem.*, **109**, 275 (1920).

Now, let the assumption be made that equation (117) expresses the activity coefficient of the hydrated ions in the more concentrated solutions.[1] Then, equation (116) becomes

$$\log \gamma = -\beta c^{\alpha'} + \left(\frac{h+j}{2}\right)\frac{c}{55.5}[i]. \qquad (118)$$

This equation has been employed to compute the following values of the activity coefficients of uniunivalent electrolytes. β and α' have been assigned the values in Table XIV. The values of $[i]$ have been computed from the values of γ_0 in Table XVII. The values of $(h+j)$ assigned to the different electrolytes are given in the table.

TABLE XXIII

OBSERVED ACTIVITY COEFFICIENTS COMPARED TO THOSE CALCULATED BY MEANS OF EQUATION (118)

c	HCl		KCl		NaCl		LiCl	
	$(h+j)=11$		$(h+j)=4$		$(h+j)=6$		$(h+j)=12$	
	γ (obs.)	γ (calc.)	γ (obs.)	γ (calc.)	γ (obs.)	γ (calc.)	γ (obs.)	γ (calc.)
0.01	0.924	0.924	0.903	0.898	0.906	0.906	0.922	0.920
0.05	0.860	0.857	0.816	0.821	0.834	0.833	0.843	0.849
0.1	0.814	0.825	0.779	0.775	0.792	0.791	0.804	0.812
0.5	0.762	0.767	0.659	0.654	0.682	0.682	0.754	0.738
1	0.823	0.823	0.613	0.592	0.652	0.652	0.776	0.784
2	1.032	(1.186)	0.566	0.559	0.672	0.679	0.936	(1.14)
3	1.35	(2.15)	0.575	0.567	0.722	(0.781)	1.20	(2.13)

The agreement between the observed and calculated values is excellent up to 1 molal concentration for the lithium chloride and hydrochloric acid, to 2 molal for sodium chloride, and to 3 molal for potassium chloride. Above these concentrations the calculated values become increasingly greater than the observed with increase in concentration. The values 4, 6, 12 for the hydration values of potassium, sodium and lithium chlorides, respectively, are in fair agreement with the values computed by Washburn[2] from transference measurements at 1 molal concentration. The value of 11 for hydrochloric acid is not in accord with that derived from these transference measurements.

There are other factors which should be mentioned in connection with this theory. It is not necessary that these hydration values should equal whole numbers, because of the

[1] Bjerrum makes this assumption but includes a factor for the change in number of solvent molecules in the solutions of different concentrations. Thus, Bjerrum employs the expression

$$\log \gamma' = -\beta c^{\alpha'} + \log \frac{55.5}{55.5 + 2c - (h+j)c}.$$

This factor will be omitted, and, therefore, we shall obtain somewhat different values from Bjerrum's for the hydration of an electrolyte.

[2] *J. Am. Chem. Soc.*, **31**, 322 (1909); Washburn and Williams, *ibid.*, **35**, 75 (1913); Washburn and Millard, *ibid.*, **37**, 694 (1915).

possibility of an ion possessing two or more hydrates in equilibrium with each other. It is also probable that the associated water molecules would react with the ions, in which case the observed hydration values would be less than the correct ones. The mean hydration values would also be a function of the concentration.

This theory affords an explanation for the minima in the activity coefficient-concentration plots of these simple electrolytes in concentrated solutions. As presented above, it leaves unexplained the variation of the activity coefficient with the concentrations in dilute solutions which may be a function of either the electrical field intensity or an equilibrium between the ions and the undissociated molecules, or both. The theory of complete ionization which Bjerrum has employed excludes the latter possibility, and makes the variation of γ in dilute solutions, represented by $\log \gamma = -\beta c^{\alpha'}$, a function of the electrostatic forces. In very dilute solutions, then, the activity coefficients of all electrolytes of the same type will approach the same value. Any differences in concentrated solutions are to be ascribed to the ionic dimensions and to ionic hydration. Further applications of this theory are to be found in the papers of Schreiner.[1]

Activities and Homogeneous Catalysis

From considerations regarding any reaction in equilibrium in solution such as

$$n_1A_1 + n_2A_2 + \cdots \rightleftharpoons n_1'A_1' + n_2'A_2' + \cdots,$$

it has been shown that the equation

$$K = \frac{a_{A_1}^{n_1'} a_{A_2}^{n_2'} \cdots}{a_{A_1}^{n_1} a_{A_2}^{n_2} \cdots} \tag{47}$$

is valid at constant temperature and pressure. Now, since such an equilibrium is a dynamic one with the opposing velocities equal, it is very probable that in the neighborhood of the equilibrium condition, the velocities in the two directions, v and v', will be

$$\left.\begin{aligned} v &= k_1 a_{A_2}^{n_1} a_{A_2}^{n_2} \cdots, \\ v' &= k_2 a_{A_1}^{n_1'} a_{A_2}^{n_2'} \cdots. \end{aligned}\right\} \tag{119}$$

This suggests that reaction velocities should be proportional to activity and activity products and not concentration and concentration products.

Indeed, before the activity function was employed, van't Hoff[2] from thermodynamic considerations regarding reaction velocities in liquid systems showed that, if the solubility of the reacting substance is taken as a unit of concentration measurement, the reaction velocities in different solvents will be independent of the nature of the medium. These conclusions, accordingly, made the reaction velocity a function of what has later been called the activity. More recently, Bugarsky[3] studied the velocity of reaction of bromine and ethyl alcohol, and attempted to evaluate the activities by measurement of

[1] *Z. anorg. Chem.*, **115**, 181 (1921); **116**, 102 (1921); **121**, 321 (1922).

[2] Lectures on Theoretical and Physical Chemistry, Arnold, London, 1898, Part I, p. 221.

[3] *Z. physik. Chem.*, **71**, 705 (1910).

the partition coefficients. Since 1918, numerous investigators [1] have employed activities and not concentrations in attempting to compute reaction velocities in aqueous solutions. The present discussion of this subject will be limited to the application of the theory to a comparatively simple case.

It is a matter of considerable difficulty to obtain a reaction catalyzed by ions which is sufficiently free from secondary influences to permit an accurate test of this principle. A reaction which has been found to conform to this theory without the introduction of any further assumptions is the conversion of acetyl-chloro-amino-benzene to para-chloro-acetanilide. This reaction is catalyzed by hydrochloric acid in aqueous solutions, and its velocity has been studied by Rivett,[2] Harned and Seltz,[3] and Åkerlöf.[4] According to the investigations of Orton and Jones,[5] its mechanism is probably well represented by the following two reactions:

$$(a)\quad C_6H_5NClCOCH_3 + H^+ + Cl^- \rightleftharpoons C_6H_5NHCOCH_3 + Cl_2,$$
$$(b)\quad C_6H_5NHCOCH_3 + Cl_2 \rightarrow p\text{-}C_6H_4ClNHCOCH_3 + H^+ + Cl^-.$$

Reaction (*a*) is slow and measurable, reaction (*b*) is very rapid, and, consequently, the hydrochloric acid concentration will remain practically constant.

If this mechanism is correct, the velocity of the reaction will be

$$v = Ka_A a_H a_{Cl}, \tag{120}$$

where a_A, a_H and a_{Cl} are the activities of the acetyl-chloro-amino-benzene, the hydrogen ion and the chloride ion, respectively. During the course of a given experiment, the concentration of the hydrochloric acid remains constant, and, therefore, $v = ka_A$. If a_A is proportional to the concentration of the acetyl-chloro-amino-benzene, the reaction will correspond to the first order equation. Consequently, from these equations, at any acid strength, we obtain

$$K = \frac{k}{a_H a_{Cl}}, \tag{121}$$

where k is the observed unimolecular velocity constant at constant temperature, pressure and acid concentration, and K is a constant at constant temperature and pressure and is independent of the acid strength.

That equation (121) holds with exactness for this reaction may be seen from Table XXIV. Column (1) contains the molal acid concentrations; column (2), the observed velocity constants from the data of Harned and Seltz; column (3), the velocity constants

[1] Harned, *J. Am. Chem. Soc.*, **40**, 1462 (1918); Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920); Åkerlöf, *Z. physik. Chem.*, **98**, 260 (1921); Scatchard, *J. Am. Chem. Soc.*, **43**, 2387 (1921); **45**, 1580 (1923); Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922); Fales and Morrel, *J. Am. Chem. Soc.*, **44**, 2071 (1922); Harned and Pfanstiel, *J. Am. Chem. Soc.*, **44**, 2194 (1922); Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); Livingston and Bray, *J. Am. Chem. Soc.*, **45**, 2048 (1923).

[2] *Z. physik. Chem.*, **82**, 201 (1913).

[3] *J. Am. Chem. Soc.*, **44**, 1475 (1922).

[4] *Medd. K. Vetenskapsakad. Nobelinstitut*, **6**, No. 2 (1922).

[5] *Rept. Brit. Assoc. Adv. Sci.*, p. 85 (1910).

divided by the square of the acid concentration; column (4), the activity coefficient of the acid computed from the electromotive force data of Ellis;[1] column (5), the square of the activity coefficient; and column (6), K of equation (121). The initial concentration of the acetyl-chloro-amino-benzene was approximately 0.02 molal. The measurements were carried out at 25°.

TABLE XXIV

VELOCITY CONSTANT-ACTIVITY RELATION OF THE REACTION
Acetyl-chloro-amino-benzene → *p*-chloro-acetanilide

(1) c	(2) k	(3) $\frac{k}{c^2}$	(4) γ	(5) γ^2	(6) $K = \frac{k}{a_H a_{Cl}}$
0.1	0.000467	0.0467	0 822	0.676	0 0692
0.2	0.001718	0.0430	0.790	0.623	0.0690
0.3	0.003756	0.04175	0.777	0.604	0.0691
0.4	0.00666	0.0416	0.773	0 598	0.0695
0.5	0.01040	0.0416	0.773	0.598	0.0695
0.6	0.01505	0.0418	0.778	0.605	0.0692
0.7	0.02104	0.04295	0.785	0.616	0.0697
0.8	0.02800	0.0438	0.795	0.632	0.0693
0.9	0.03660	0.0448	0.807	0.651	0.0694
1	0.0465	0.0465	0.820	0.672	0.0692

The constancy of the values in the last column of the table are a complete corroboration of equation (121).[2] It is important to note that the values of k/c^2 as well as γ and γ^2 pass through minimum values at identical acid concentrations. Equation (121) holds in the range of acid concentrations from dilute solutions to 1 molal and above.

The above example shows that the activities should serve as a basis for the calculation of reaction velocities in liquid systems and homogeneous catalysis. The problem becomes much more complicated for reactions other than the simple one just discussed, because most reactions in solutions are catalyzed by the individual ions. In order to obtain a knowledge of individual ion activities, we are confronted with all the difficulties accompanying the elimination or calculation of liquid junction potentials. Other factors which may cause departures from the simple theory have been discussed in the interesting recent investigations of W. C. McC. Lewis and his colleagues, Bronsted, Scatchard, and others, to whom reference has been made.

CELLS WITH LIQUID JUNCTIONS. CALCULATION OF TRANSFERENCE NUMBERS. LIQUID JUNCTION POTENTIALS

The cell without liquid junction is the only type which has been considered, and it has been shown that from measurements of such cells the activity products and mean activity coefficients may be computed with exactness. We have yet to consider the very difficult and important problems of the cell with a liquid junction.

The electromotive force, **E**, of the cell

$$Li_xHg\,|LiCl\ (c')\,|LiCl\ (c'')\,|\,Li_xHg$$

[1] *J. Am. Chem. Soc.*, **38**, 737 (1916).

[2] This does not constitute a proof of the reaction mechanism given above, which is one of a number of possible mechanisms from which equation (121) might have been deduced.

where c'' is greater than c', is equal to the sum of the two electrode potentials and the potential at the liquid junction of the two solutions. Therefore,

$$\mathbf{E} = \frac{RT}{\mathbf{F}} ln \frac{a'}{a''} + \mathbf{E}_1, \tag{122}$$

where a' and a'' are the activities of the lithium ion at concentrations c' and c'', respectively, and $\mathbf{E}_1$ is the liquid junction potential. If, therefore, $\mathbf{E}_1$ could be evaluated, it would be possible to determine the activity of the lithium ion. There are no a priori reasons nor any facts which would indicate that the activity of the lithium and chloride ions should be identical in a lithium chloride solution of a given strength. The electromotive force method would be a powerful means of investigating individual ion activities, if the problem of liquid junction potentials could be adequately solved. Although almost all purely thermodynamic calculations can be made from a knowledge of ion activity products, and not individual ion activities, the determination of the individual ion activities is of paramount importance for the theory of solutions. Thermodynamics offers valuable aid in the study of liquid junction potentials, but it is not possible by thermodynamic methods alone to evaluate liquid junction potentials, since a knowledge of individual ion activities would be required. We are thus confronted with the interesting perplexity that it is not possible to compute liquid junction potentials without a knowledge of individual ion activities, and it is not possible to determine individual ion activities without an exact knowledge of liquid junction potentials. For the solution of this difficult problem, it is necessary to go outside the domain of exact thermodynamics.

Liquid junction potentials are produced by the process of diffusion. Consider the boundary

HCl (conc.) |HCl (dil.).

There will be a tendency for the acid to diffuse from the concentrated to the dilute solution, and, since the hydrogen ion has a higher mobility than the chloride ion, an excess of hydrogen ions will diffuse into the dilute solution until a sufficient electromotive force is set up to retard enough hydrogen ions and accelerate enough chloride ions to equalize the diffusion rates. The net result will be an electromotive force from the more concentrated to the more dilute solution. Similar reasoning may also be applied to the boundary

LiCl (c) |HCl (c).

Since the hydrogen ion has a higher mobility than the lithium ion, the lithium chloride solution is first charged positively to the hydrochloric acid solution, and, in consequence, an electromotive force will be set up which is directed from the hydrochloric acid to the lithium chloride solution.

Concentration Cells with Liquid Junction: For the purpose of concreteness, let us consider the cell

Hg |HgCl |HCl (c') |HCl (c'') |HgCl |Hg.

Let 1 Faraday of electricity pass through the cell. n_c gram equivalents of hydrogen ion will pass in one direction, and n_a gram equivalents of chloride ion will pass in the other direction across the boundary where n_c and n_a are the cation and anion transference numbers, respectively. The decreases in free energy of the cation and anion at the boundary will be, respectively, during such a reversible change,

$$\left.\begin{aligned} n_c\mathbf{F}\int_{c''}^{c'} d\mathbf{E}_1 &= n_cRT\int_{c''}^{c'} dlna_+, \\ n_a\mathbf{F}\int_{c''}^{c'} d\mathbf{E}_1 &= -n_aRT\int_{c''}^{c'} dlna_-. \end{aligned}\right\} \tag{123}$$

Since $(n_c + n_a)$ equals unity, the sum of these will be

$$\mathbf{F}\int_{c''}^{c'} d\mathbf{E}_1 = n_cRT\int_{c''}^{c'} dlna_+ - n_aRT\int_{c''}^{c'} dlna_-,$$

whence the liquid junction potential may be obtained by integration. Therefore,

$$\mathbf{E}_1 = \frac{RT}{\mathbf{F}}\left[n_c ln\frac{a_+'}{a_+''} - n_a ln\frac{a_-'}{a_-''}\right], \tag{124}$$

which is a general formula for the liquid junction potential for this type of cell. The total electromotive force will be according to (122)

$$\mathbf{E}_T = \frac{RT}{\mathbf{F}} ln\frac{a_-'}{a_-''} + \mathbf{E}_1 \tag{122}$$

$$= \frac{RT}{\mathbf{F}}\left[n_c ln\frac{a_+'}{a_+''} + (1 - n_a) ln\frac{a_-'}{a_-''}\right]$$

$$= \frac{RTn_c}{\mathbf{F}} ln\frac{a_+'a_-'}{a_+''a_-''}$$

$$= \frac{RT2n_c}{\mathbf{F}} ln\frac{\sqrt{a_+'a_-'}}{\sqrt{a_+''a_-''}}. \tag{125}$$

This is the exact equation for a concentration cell of the above type with liquid junction.

The equation for the electromotive force of concentration cells without liquid junction has been shown to be

$$\mathbf{E} = \frac{2RT}{\mathbf{F}} ln\frac{\sqrt{a_+'a_-'}}{\sqrt{a_+''a_-''}}, \tag{49}$$

when the solutions contain uniunivalent electrolytes. By combining this equation with (125), we obtain the exact and simple equation

$$\mathbf{E}_T = n_c\mathbf{E}. \tag{126}$$

This equation may be very successfully employed for the determination of the average transference number between the concentrations c' and c''.

If it be assumed that the cation and anion activities are equal, equation (124) becomes

$$\mathbf{E}_1 = (n_c - n_a)\frac{RT}{\mathbf{F}} ln \frac{a_+'}{a_+''}, \tag{127}$$

which becomes

$$\mathbf{E}_1 = (n_c - n_a)\frac{RT}{\mathbf{F}} ln \frac{c'}{c''}, \tag{127a}$$

in very dilute solutions. This last equation, which was first obtained by Nernst,[1] rests on the assumption that both ions have equal activities and that the activity ratio equals the concentration ratio. It can, therefore, only be valid as a limiting law in very dilute solutions.

On the assumption that the cation and anion activities are equal, and from equations (124) and (125), it is found that

$$\mathbf{E}_1 = \mathbf{E}_T\left(1 - \frac{1}{2n_c}\right). \tag{128}$$ [2]

From these deductions, many of the difficulties in calculating liquid junction potentials become obvious. Equation (124), which is exact, cannot be employed without a knowledge of individual ion activities. Equation (128) is based on an arbitrary assumption that the cation and anion activities are equal in a solution of a uniunivalent electrolyte of a given strength. The Nernst formula involves the difficulties accompanying the determination of the ion concentrations of strong electrolytes, and only approaches validity as the concentration approaches zero.

The Determination of Transference Numbers from Electromotive Force Measurements: As a result of these derivations, it was found that equation (126) is an exact expression which may be used to obtain the mean transference numbers between two concentrations from measurements of concentration cells with and without liquid junctions.[3] The method has been recently employed with considerable success by MacInnes and Parker [4] in the case of potassium chloride solutions, MacInnes and Beattie [5] for lithium chloride solutions, and Pearce and Hart [6] for potassium bromide solutions. However, since the transference numbers of most ions vary considerably with change in concentration, it is more desirable to obtain the transference number at a given concentration. To accomplish this, we may differentiate (126) and obtain

$$d\mathbf{E}_T = n_c d\mathbf{E}. \tag{129}$$

[1] *Z. physik. Chem.*, **4**, 129 (1889).
[2] MacInnes, *J. Am. Chem. Soc.*, **37**, 2301 (1915).
[3] First suggested by Helmholtz, *Ges. Abhl.*, **1**, 840; **2**, 979.
[4] *J. Am. Chem. Soc.*, **37**, 1445 (1915); also Beattie, *J. Am. Chem. Soc.*, **42**, 1128 (1920).
[5] *J. Am. Chem. Soc.*, **42**, 1117 (1920).
[6] *J. Am. Chem. Soc.*, **43**, 2483 (1921).

If $\mathbf{E}_T$ be plotted against corresponding values of $\mathbf{E}$, of concentration cells of which one concentration is fixed and the other varied, the slope of the curve obtained will be the cation transference number. By employing a similar method, MacInnes and Beattie determined the transference numbers of lithium ion from measurements of the cells

$$\text{Ag}\,|\text{AgCl}\,|\text{LiCl}\ (c_1)\,|\text{LiCl}\ (c_2)\,|\text{AgCl}\,|\text{Ag}$$

and

$$\text{Ag}\,|\text{AgCl}\,|\text{LiCl}\ (c_1)\,|\text{Li}_x\text{Hg}\,|\text{LiCl}\ (c_2)\,|\text{AgCl}\,|\text{Ag}.$$

In Table XXV are given their values, which are compared with values obtained by the Hittorf method.[1]

TABLE XXV

TRANSFERENCE NUMBERS OF THE LITHIUM ION IN SOLUTIONS OF LITHIUM CHLORIDE

c	n_c (E.M.F.)	n_c (Hittorf)
0.001	0.359	—
0.005	0.341	—
0.01	0.334	0.332
0.02	0.327	0.328
0.05	0.318	0.320
0.1	0.311	0.313
0.2	0.304	0.304
0.3	0.299	0.299
0.5	0.293	—
1	0.286	—
2	0.276	—
3	0.268	—

The agreement is very striking. It seems probable from this and other similar results that the electromotive force method, when applicable, is the most accurate way available for the determination of transference numbers.

Further Considerations of Liquid Junction Potentials: Equation (127*a*), which is a limiting law, valid in very dilute solutions, for the liquid junction potential between two solutions of the same electrolyte at different concentrations, was deduced by Nernst[2] from his osmotic theory of the cell. On the basis of the osmotic theory of Nernst, Planck[3] deduced a general equation for any kind of liquid junction potential. One feature of Planck's deduction was that he assumed an initially sharp boundary between the solutions, as a result of which the mixing could only take place by diffusion. Henderson[4] also deduced a general equation but on the assumption of an initial mixing at the boundary. The Henderson equation for this reason gives for most types of boundaries values different from the Planck equation.

[1] Noyes and Falk, *J. Am. Chem. Soc.*, **33**, 1436 (1911).
[2] *Z. physik. Chem.*, **2**, 613 (1888); **4**, 129 (1889).
[3] *Wied. Ann.*, **39**, 161 (1890); **40**, 561 (1890).
[4] *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

These formulas of Planck and Henderson, because of the doubtful nature of the assumptions from which they are derived, could only yield approximate results even in dilute solutions. Ionic concentrations and ionic mobilities occur in their equations, and the values of these quantities are not known in solutions at all concentrated.

Planck and later Henderson obtained the same equation for the liquid junction potential between two solutions of different electrolytes having a common ion and at the same concentration. The Planck equation is

$$\mathbf{E}_1 = \frac{RT}{\mathbf{NF}} ln \frac{U_c' + U_a}{U_c'' + U_a} \tag{130}$$

for the case of a common anion. Lewis and Sargent [1] modified this equation by substituting the molecular conductance ratio for the ratio of the sums of the mobilities. Such a procedure would undoubtedly diminish an error caused by a change in the mobilities with a change in concentration. They accordingly obtained for uniunivalent electrolytes

$$\mathbf{E}_1 = \frac{RT}{\mathbf{F}} ln \frac{\Lambda_1}{\Lambda_2} \tag{131}$$

for the case of the common anion, and

$$\mathbf{E}_1 = -\frac{RT}{\mathbf{F}} ln \frac{\Lambda_1}{\Lambda_2} \tag{132}$$

in case the cation was common to both electrolytes.

A simple deduction of Lewis and Sargent's formula which has recently been made by MacInnes and Yeh [2] illustrates the kind of reasoning and the types of assumptions which have led to liquid junction potential formulas, and this deduction will be reproduced here. Consider the boundary

$$\text{HCl } (c) \,|\, \text{KCl } (c),$$

which is representative of any boundary between uniunivalent electrolyte solutions with a common anion. We shall make Henderson's assumption, that at the boundary, where the two solutions meet, there will be a layer in which the concentrations vary from pure potassium chloride to pure hydrochloric acid Imagine a plane in this layer. If x equals the concentration of the hydrochloric acid in this layer, then $(c - x)$ will be the potassium chloride concentration. In a plane at a distance dl from this plane, $(x + dx)$ will be the acid concentration, and $c - (x + dx)$ the chloride concentration. The decrease in free energy accompanying the passage of one Faraday will be

$$(-\Delta\mathbf{F}) = \mathbf{F}d\mathbf{E}_1 = -RT(n_{\mathrm{K}} dlna_{\mathrm{K}} + n_{\mathrm{H}} dlna_{\mathrm{H}} - n_{\mathrm{Cl}} dlna_{\mathrm{Cl}}). \tag{133}$$

[1] *J. Am. Chem. Soc.*, **31**, 363 (1909).
[2] *J. Am. Chem. Soc.*, **43**, 2563 (1921).

n_K, n_H, n_{Cl} are the transference numbers; a_K, a_H, a_{Cl} are the activities of the ions denoted by subscripts. Let the assumption be made that the chloride ion in the acid solution has the same activity as it has in the salt solution at the concentration c. Then, $dlna_{Cl}$ equals zero. The transference numbers in the plane will be

$$n_H = \frac{\frac{x}{c}\Lambda_H}{\frac{x}{c}\Lambda_H + \frac{c-x}{c}\Lambda_K + \Lambda_{Cl}}$$

and

$$n_K = \frac{\left(\frac{c-x}{c}\right)\Lambda_K}{\frac{x}{c}\Lambda_H + \left(\frac{c-x}{c}\right)\Lambda_K + \Lambda_{Cl}},$$

where Λ_H, Λ_K, and Λ_{Cl} are the equivalent conductances of the ions. Further, let $\frac{x}{c} = l$, and, consequently, $\frac{c-x}{c} = 1 - l$, whence

$$\left.\begin{aligned} n_H &= \frac{l\Lambda_H}{l\Lambda_H + (1-l)\Lambda_K + \Lambda_{Cl}} \\ \text{and} \qquad n_K &= \frac{(1-l)\Lambda_K}{l\Lambda_H + (1-l)\Lambda_K + \Lambda_{Cl}}. \end{aligned}\right\} \tag{134}$$

Now, let the approximate assumption be made that, at low concentrations, a_H is proportional to x and a_K is proportional to $(c - x)$. Then

$$\left.\begin{aligned} dlna_H &= dlnl = \frac{dl}{l}, \\ dlna_K &= -dln(1-l) = -\frac{dl}{(1-l)}. \end{aligned}\right\} \tag{135}$$

Combining equations (133), (134), and (135), we obtain

$$\mathbf{F}d\mathbf{E}_1 = -\frac{RT(\Lambda_H - \Lambda_K)dl}{l(\Lambda_H - \Lambda_K) + \Lambda_K + \Lambda_{Cl}}. \tag{136}$$

Let $\Lambda_H - \Lambda_K = \alpha$, and $\Lambda_K + \Lambda_{Cl} = \beta$, and integrate between $l = 0$ and $l = 1$. We obtain

$$\mathbf{E}_1 = -\frac{RT}{\mathbf{F}}\int_1^0 \frac{dl}{\left(l + \frac{\beta}{\alpha}\right)} = -\frac{RT}{\mathbf{F}}\left[ln\left(l + \frac{\beta}{\alpha}\right)\right]_1^0 \tag{137}$$

or

$$\mathbf{E}_1 = \frac{RT}{\mathbf{F}} ln \frac{\Lambda_H + \Lambda_{Cl}}{\Lambda_K + \Lambda_{Cl}}, \tag{131}$$

which is Lewis and Sargent's formula.

Many difficulties are encountered in the measurements of liquid junction potentials. In the first place, the values observed by different investigators differ, because of the different methods employed in establishing the liquid junctions. Little difficulty has been encountered in reproducing the electromotive forces of cells in which the liquid junction is between two solutions of the same electrolyte at different concentrations. The situation is quite otherwise with many cells in which the liquid junction is found between solutions of different electrolytes. A careful investigation of the methods of establishing liquid junctions was made by Lewis, Brighton and Sebastian.[1] They finally employed a method whereby the two solutions were joined by dipping a tube containing one solution into a wider tube containing the other solution, and observed that, although the liquid junction potentials varied during the first few seconds, they soon reached a constant value. Lamb and Larson [2] have shown that many factors affect liquid junction potential measurements, and have found that a junction formed by two flowing solutions gave much more reproducible results than any other kind of junction yet investigated. The flowing junction may have a potential somewhat different from the stationary junction. The magnitude of this difference and the applicability of Lewis and Sargent's formula are illustrated in Table XXVI in which are included some of the measurements by MacInnes and Yeh [3] and Lewis, Brighton, and Sebastian [1] on cells of the type

$$Ag|AgCl|MCl\ (c)|M'Cl\ (c)|AgCl|Ag,$$

where M and M′ are univalent cations. If the activities of the chloride ion are the same in the two solutions, it is clear that the total electromotive force of the cell is equal to the liquid junction potential. MacInnes and Yeh (M. and Y.) employed the flowing junction method, while the observations of Lewis, Brighton and Sebastian (L., B. and S.) were made on stationary junctions. In the last column are given the values computed by Lewis and Sargent's formula.

TABLE XXVI

POTENTIALS IN MILLIVOLTS AT JUNCTIONS OF UNIUNIVALENT CHLORIDE SOLUTIONS AT 25°

Junction	E.M.F. (Obs.) (M. and Y.) Flowing	E.M.F. (Obs.) (L., B. and S.) Stationary	E.M.F. (Calc.) Lewis and Sargent's Equation
HCl (0.1) | KCl (0.1)	26.8	27.8	28.4
HCl (0.01) | KCl (0.01)	25.7	27.2	27.4
HCl (0.1) | LiCl (0.1)	34.9	—	35.8
HCl (0.1) | NH_4Cl (0.1)	28.4	—	28.6
KCl (0.1) | NaCl (0.1)	6.4	—	4.9
NaCl (0.1) | LiCl (0.1)	2.6	—	2.5
HCl (0.01) | NH_4Cl (0.01) . .	27.0	—	27.4
HCl (0.01) | LiCl (0.01)	33.8	—	34.2
KCl (0.01) | NH_4Cl (0.01) . .	1.3	—	0.05

[1] *J. Am. Chem. Soc.*, **39**, 2245 (1917).
[2] *J. Am. Chem. Soc.*, **42**, 229 (1920).
[3] *J. Am. Chem. Soc.*, **43**, 2563 (1921).

A comparison of the results obtained by the flowing and stationary junctions shows of how great importance is the method of forming the junction. The values computed by Lewis and Sargent's formula agree well with the observed values obtained by MacInnes and Yeh except in the cases where potassium chloride solutions were used. This peculiar behavior has not yet been explained. It would appear from these results that the Lewis and Sargent formula may be relied on to give results which will probably not be in error by over one millivolt in dilute solutions.

In an attempt to surmount the numerous difficulties, it has been customary to interpose at the liquid junction a saturated solution of some electrolyte whose ions have as nearly as possible the same mobility. Of these "salt bridges," a solution of saturated potassium chloride has proved the most successful. All determinations of hydrogen ion activities, or of p_H values,[1] recently employed very extensively in bio-chemical studies, have been obtained by employing a hydrogen electrode and a saturated potassium chloride bridge. By this means the liquid junction potential is considerably reduced, but it is not eliminated, and remains undetermined.[2] Although only results of undetermined exactness may be obtained by this method, it is possible by obtaining a large number of results of many cell combinations to arrive at certain important but approximate conclusions regarding the individual activities of some of the ions.

Individual Ion Activities

From measurements of freezing point lowerings, of concentration cells without liquid junctions, or of vapor pressure lowerings of the solutions of electrolytes, it is possible to compute only the products of ion activities, or the mean activity coefficients of the electrolytes. Such measurements give no information regarding the individual activities or activity coefficients of the ions. A knowledge of the individual ion activities is of no value in thermodynamic calculations which involve an entire cell reaction. On the other hand, such a knowledge is very important in fields of investigation, like hydrogen ion catalysis, which involve specific ionic action.

In most of the earlier calculations of the thermodynamic properties of solutions, it has been tacitly assumed without proof (2) that the thermodynamic coefficients of two ions of a uniunivalent electrolyte in a given solution were identical. Both the ions, for example, were assumed to have the same van't Hoff coefficient, as long as this quantity was assumed to measure a degree of dissociation. It is clear from the relation between the activity and the van't

[1] $\left(p_H = \log \frac{1}{a_H} = \log \frac{1}{[H]} \right)$.

[2] Recent accurate studies of cells containing saturated potassium chloride for the elimination of liquid junction potentials have been made by Bjerrum, *Z. physik. Chem.*, **53**, 429 (1905); *Z. Elektrochem.*, **17**, 58, 389 (1911), Harned, *J. Am. Chem. Soc.*, **37**, 2460 (1915), Fales and Vosburgh, *J. Am. Chem. Soc.*, **40**, 1302 (1918), Fales and Mudge, *J. Am. Chem. Soc.*, **42**, 2434 (1920), Åkerlöf, *Medd. K. Vetenskapsakad. Nobelinstitut*, **6**, No. 2 (1922), and others.

Hoff coefficients that if the activity coefficients of the ions of an electrolyte differ in a given solution, then the van't Hoff coefficients would also differ. Since we would not consider either the partial volumes, partial specific heats, or partial heat contents of the ions of an electrolyte at a given concentration to be equal, there is no a priori reason for considering their partial free energies identical.

The properties of dilute solutions of strong electrolytes are strikingly additive. The additivity of the refractive indices, rotatory powers, specific heats, and partial volumes is well known. As pointed out by Lewis,[1] this striking additivity of the properties of the ions, along with the identity of the heat of neutralization of strong acids and bases, may be used as an argument for the theory of complete dissociation of strong electrolytes. More recently, MacInnes [2] has pointed out some other striking additivity relationships, particularly of the ionic conductances. In Table XXVII are given the values of the ionic

TABLE XXVII

IONIC CONDUCTANCES OF THE CHLORIDE ION IN SOLUTIONS OF UNIUNIVALENT CHLORIDES AT DIFFERENT CONCENTRATIONS AND 18°

c	0.01		0.1		0.2		1	
	$n_{Cl}\Lambda$	$n_{Cl}\Lambda\eta^{0.7}$	$n_{Cl}\Lambda$	$n_{Cl}\Lambda\eta^{0.7}$	$n_{Cl}\Lambda$	$n_{Cl}\Lambda\eta^{0.7}$	$n_{Cl}\Lambda$	$n_{Cl}\Lambda\eta^{0.7}$
HCl..	61.67	61.67	56.6	56.8	54.4	54.8	46.95	48.6
CsCl.	61.89	61.89	56.6	56.5	—	—	—	—
KCl	61.68	61.68	56.45	56.4	54.4	54.3	49.50	48.8
NaCl	61.55	61.55	56.67	57.0	54.2	54.8	45.9	48.6
LiCl..	61.46	61.48	56.35	56.95	53.8	54.9	43.9	48.5

conductance of the chloride ion in solutions of hydrochloric acid, cæsium, potassium, sodium and lithium chloride solutions calculated by MacInnes at concentrations from 0.01 to 1 molal. n_{Cl} is the chloride ion transference number, Λ the [illegible] conductance and η the viscosity. At the lower concentrations, [illegible] conductance of the chloride ion without the viscosity correction, $n_{Cl}\Lambda$, is very nearly the same in solutions of all these electrolytes. At the higher concentrations, MacInnes has introduced an empirical viscosity correction, which makes the ionic conductance, in a solution which has unit relative viscosity, equal $n_{Cl}\Lambda\eta^{0.7}$. The values of these corrected ionic conductances of the chloride ion are the same in solutions as concentrated as 1 normal.

From such considerations, MacInnes adopted the plausible assumption that, in dilute solutions of potassium chloride and hydrochloric acid at the same molal concentration, the chloride ion will have the same activity. This

[1] *Z. physik. Chem.*, **70**, 212 (1909).

[2] *J. Am. Chem. Soc.*, **41**, 1086 (1919); **43**, 1217 (1921).

is simply an extension of the principle of the additivity of ionic properties to include the partial free energies of the ions, or the logarithms of the ion activities. MacInnes further assumed that in a dilute solution of potassium chloride at a given strength the potassium and chloride ions possess identical activities. If the additivity principle and this latter assumption are valid, then it will be possible to compute the individual ion activities.

Any evidence for or against these assumptions should be obtained from thermodynamic data. It was shown in the last section that the difficulty of determining individual ion activities and activity coefficients from electromotive force data depends on the present lack of accurate methods of computing liquid junction potentials, and, consequently, the best method at present available is to employ a saturated solution of potassium chloride for the purpose of diminishing the liquid junction potential.

From measurements of cells of the type

$$H_2 \,|\, MeCl_x\ (c) + HCl\ (0.1) \,|\, (sat.)\ KCl \,|\, \text{calomel electrode},$$

where $MeCl_x$ was an alkali or an alkaline earth chloride, Harned[1] obtained evidence that the hydrogen ion activity of the acid was increased by the addition of the salts. Let $\mathbf{E}_0(1)$ and $\mathbf{E}(1)$ equal the electromotive forces of this cell when c equals zero, and c equals a positive value, respectively. Now, if the difference in liquid junction potentials at the boundaries

$$HCl\ (0.1) \,|\, \text{sat. KCl} \quad \text{and} \quad KCl\ (c) + HCl\ (0.1) \,|\, \text{sat. KCl}$$

is zero, then

$$\mathbf{E}' = \mathbf{E}_0(1) - \mathbf{E}(1) = \frac{RT}{\mathbf{F}} ln \frac{a_{H(s)}}{a_{H(0.1)}}, \tag{138}$$

where $a_{H(s)}$ is the activity of the hydrogen ion in the salt solution. From measurements of cells of the type

$$H_2 \,|\, MeCl\ (c) + HCl\ (0.1) \,|\, HgCl \,|\, Hg,$$

where Me represents potassium, sodium, or lithium, the product $a_{H(s)}a_{Cl}$ in the solutions may be calculated. Thus, if $\mathbf{E}_0(2)$ and $\mathbf{E}(2)$ are the electromotive forces of this latter cell without and with salt present, respectively, we obtain

$$\mathbf{E}'' = \mathbf{E}_0(2) - \mathbf{E}(2) = \frac{RT}{\mathbf{F}} ln \frac{a_{H(s)}a_{Cl(c+0.1)}}{a_{H(0.1)}a_{Cl(0.1)}}. \tag{139}$$

From these two equations, it follows that

$$\mathbf{E}'' - \mathbf{E}' = \frac{RT}{\mathbf{F}} ln \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}. \tag{140}$$

This equation could only be exact if the liquid junction potentials mentioned

[1] *J. Am. Chem. Soc.*, **37**, 2460 (1915).

above are zero. We have already found that, in a solution of the same concentrations of lithium, sodium and potassium chlorides,

$$a_{Li}a_{Cl} > a_{Na}a_{Cl} > a_{K}a_{Cl},$$

where a_{Li}, a_{Na}, a_{K} and a_{Cl} are the activities of the ions denoted by subscripts. Thus, if $(E'' - E')$ is the same in the mixtures, we have good evidence that the chloride ion activity is the same in all the solutions, and that, consequently,

$$a_{Li} > a_{Na} > a_{K}$$

in solutions of the same molal concentrations of the chlorides. In Table XXVIII are given the results Harned obtained from cells of the above types.

TABLE XXVIII

EVIDENCE FROM ELECTROMOTIVE FORCE DATA THAT THE CHLORIDE ION ACTIVITY IS THE SAME IN SOLUTIONS OF UNIUNIVALENT CHLORIDES AT A GIVEN CONCENTRATION

Added Salt	$c\left(\frac{\text{mols.}}{\text{liter}}\right)$	E''	E'	$\frac{RT}{F} ln \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}$
KCl	0.2	0.0247	0.0003	0.0244
	0.5	0.0416	0.0012	0.0404
	1	0.0587	0.0033	0.0554
	2	0.0828	0.0104	0.0724
	3	0.1026	0.0192	0.0834
NaCl	0.2	0.0252	0.0011	0.0241
	0.5	0.0431	0.0030	0.0401
	1	0.0618	0.0070	0.0548
	2	0.0888	0.0176	0.0712
	3	0.1121	0.0300	0.0821
LiCl	0.2	0.0264	0.0020	0.0244
	0.5	0.0452	0.0052	0.0400
	1	0.0661	0.0106	0.0555
	2	0.0966	0.0248	0.0718
	2.5	0.1110	0.0337	0.0773[a]
	3	—	—	(0.0826)[b]

(*a*) Falls on E.M.F.—*c* plot of potassium and sodium chloride results.

(*b*) Extrapolated graphically.

The agreement of the results in the last column is striking even in solutions of very high concentrations. The maximum deviation is 1.3 millivolts which would correspond to approximately a deviation of 4 per cent in the activity coefficient of the chloride ion. It seems probable from these results that the chloride ion has the same activity in solutions of the same concentration of chlorides of the same type.

By the same method, Harned and Brumbaugh [2] obtained similar results for the activities of the chloride ion in 0.1 molal hydrochloric acid solutions containing calcium, strontium and barium chlorides, from which they concluded that in solutions of these biunivalent

[2] *J. Am. Chem. Soc.*, **44**, 2729 (1922).

chlorides at a given concentration the chloride ion activity is the same up to 1 molal concentration. The activity of the chloride ion in the uniunivalent chloride solutions is greater than in the biunivalent chlorides at the same equivalent weight concentration. It should be pointed out that these conclusions will not be strictly true if it can be shown that the liquid junction potentials involved are of an order of magnitude greater than 1 millivolt. The assumption of the equality of the activity of the chloride ion and the assumption that these liquid junction potential differences are nearly equal to zero are equivalent. To sum up the matter, it seems probable from this series of results that this postulate which MacInnes introduced for dilute solutions is very exact in dilute solutions of chlorides, and may become less valid in concentrated solutions. It is also probable that it can be extended to dilute solutions of other electrolytes.

From the mean values in the last column of Table XXVIII, a test may be made of the assumption that in a solution of potassium chloride at a given concentration the potassium and chloride ion activities are equal. Thus, $\frac{RT}{\mathbf{F}} ln \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}$ will equal one half the electromotive force of cells without liquid junction of the type

$$Hg\,|HgCl\,|KCl\ (c + 0.1)\,|Hg_xK\,|KCl\ (0.1)\,|HgCl\,|Hg,$$

if a_K equals a_{Cl} at a given concentration. The electromotive force of this cell, $\mathbf{E}_{KCl}$, is given by

$$\mathbf{E}_{KCl} = 0.05915 \log \frac{a_{K(c+0.1)} a_{Cl(c+0.1)}}{a_{K(0.1)} a_{Cl(0.1)}}$$

at 25°, and, if a_K equals a_{Cl},

$$\mathbf{E}_{KCl} = 0.05915 \times 2 \log \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}.$$

Therefore, if the values of $\frac{1}{2}\mathbf{E}_{KCl}$ equal the corresponding value in the last column of Table XXVIII, evidence will be obtained for the equality of a_K and a_{Cl} in a solution of a given concentration. The results obtained by Harned are given in Table XXIX. The column headings require no further explanation.

TABLE XXIX

EVIDENCE FOR THE IDENTITY OF THE ACTIVITIES OF THE POTASSIUM AND CHLORIDE IONS IN SOLUTIONS OF POTASSIUM CHLORIDE

$(c + 0.1)$ mols / liter	$\frac{RT}{\mathbf{F}} ln \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}$ (Table XXVIII)	$\frac{1}{2}\mathbf{E}_{KCl}$.	Diff.
0.3	0.0243	0.0250	0.0007
0.6	0.0402	0.0412	0.0010
1.1	0.0552	0.0557	0.0005
2.1	0.0718	0.0720	0.0002
3.1	0.0827	0.0825	−0.0002

The small magnitude of the differences in the last column is evidence that a_K and a_{Cl} are the same, or nearly the same, at a given concentration even in solutions of high concentrations. The differences in the last column might very easily be caused by an error made regarding the liquid potential differences involved.

There are no other electromotive force data of this kind at present available on other mixtures which may be employed to throw further light on this interesting subject. As far as these data are concerned, evidence has been obtained for three useful postulates.

1. In solutions of electrolytes, the activities of the cation and anion, respectively, may differ in a solution of a given concentration.

2. In solutions of uniunivalent chlorides at a given concentration, the chloride ion activities are the same. In solutions of calcium, strontium, and barium chlorides at a given concentration, the chloride ion activities are the same.

3. In a solution of potassium chloride of a given concentration, the activities of the chloride and potassium ions are identical.

On the assumption of these postulates, Lewis and Randall [1] have computed the individual ion activity coefficients of many ions of different types up to an ionic strength of 0.1. Harned [2] has computed the individual ion activity coefficients of the uniunivalent chlorides and hydrochloric acid by the use of these postulates even up to high concentrations, and also the hydrogen ion activities of 0.1 molal hydrochloric acid in solutions of uniunivalent and unibivalent chlorides. According to these latter calculations, the hydrogen ion activity of the 0.1 molal acid is increased by all of these salts, and the increase is greater in lithium chloride than in sodium or potassium chloride solutions.

In the earlier investigations, and according to the classic theory of electrolytes, it was always assumed that in a solution of a strong electrolyte at a given concentration the cation and anion have the same activity coefficient. This assumption seems to be inadequate to account for either the simplest behaviors of electrolytes or their mixtures. The postulate that the activity coefficients of the cation and anion may differ in a given solution, and consequently their van't Hoff and osmotic coefficients, has found support in the work of a number of investigators.[3] One result of the theory of complete dissociation as developed by Debye and Hückel is that the partial free energies, logarithms of the activities, and the osmotic coefficients of ions of a given valence type in solutions of electrolytes of the same valence type should be additive. This is the case if these thermodynamic quantities are functions of the electrostatic field strength and ionic dimensions only. It will not be the case if reactions of any kind take place between the ions. From the results just recorded, it would appear that, for the very simple ions, very marked

[1] *J. Am. Chem. Soc.*, **43**, 1112 (1921).

[2] *J. Am. Chem. Soc.*, **42**, 1808 (1920); **44**, 252 (1922).

[3] MacInnes, *J. Am. Chem. Soc.*, **41**, 1086 (1919); Harned, *J. Am. Chem. Soc.*, **42**, 1808 (1920); Pearce and Hart, *J. Am. Chem. Soc.*, **43**, 2483 (1921); Lewis and Randall, *J. Am. Chem. Soc*, **43**, 1112 (1921); Brönsted, *J. Am. Chem. Soc.*, **44**, 877 (1922); Corran and Lewis, *J. Am. Chem. Soc.*, **44**, 1673 (1922).

additivity of the partial free energies is observable, even in the concentrated solutions. The second of the above postulates would appear to hold for the ions of the alkali metals and halide ions in solutions of uniunivalent halides; and the alkaline earth metal ions and halide ions in solutions of biunivalent halides with great exactness in the dilute solutions, and to be an unexpectedly close approximation in the concentrated solutions. On the other hand, this principle is not valid for the nitrate ion and other complex ions. This point has been emphasized by Brönsted.[1] The equilibria resulting from the presence of undissociated molecules, secondary dissociation of complex ions, or "secondary electrical interactions" between the ions may be the cause of the departure from the principle of additivity of partial free energies.

The most extensive investigations of the action of ions on the activity coefficients of other ions has been made by Brönsted [2] who has found many varied specific behaviors in dilute solutions of complex electrolytes of various valence types in solutions of other electrolytes. These studies have led him to propose a general theory of ionic interaction that "in a dilute salt solution of constant total concentration, ions will be uniformly influenced by ions of their own sign." The theory upon which this principle rests is that in dilute solutions specific electrical reactions take place between the ions. In dilute solutions, only those ions of unlike sign would approach closely enough to each other to produce such an effect. The equations deducible from this principle have been shown by Brönsted to agree in a very striking manner with many varied experimental results in dilute solutions.

As a result of these different investigations, it would appear that the activity coefficient of an ion at constant temperature is a function of its concentration, its valence, its dimensions, its complexity, and its interaction with the other ions in the solution containing it. At higher concentrations, the effect of hydration becomes prominent as a factor which probably causes the thermodynamic behaviors of the ions to differ.

All those who have been engaged in this field recognize the great difficulties and the conjectural nature of the assumptions and values obtained. The investigations mentioned in this discussion represent the most determined attempt to unravel this complicated question. The conclusions are to be regarded tentatively, and subject, if necessary, to change, as a result of further accumulation of evidence or new methods of attack. Finally, it should be emphasized that many of the problems of solutions, in the fields of homogeneous catalysis, studies of single electrodes, solubilities of salts in salt solutions, and liquid junction potentials, await for their answers upon a more accurate knowledge of the thermodynamic properties of the individual ions. Such studies have merely begun.

Standard Electrode Potentials

On account of the very important properties of the free energy, the determination of the free energies of chemical substances and the free energy increments of reactions constitutes one of the most important and useful de-

[1] Brönsted, *J. Am. Chem. Soc.*, **45**, 2898 (1923).

[2] Brönsted, *J. Am. Chem. Soc.*, **42**, 761 (1920); **44**, 877 (1922); etc.

velopments in chemistry. It has previously been shown that measurements of the electromotive forces of galvanic cells under conditions of reversibility afford a very important means of obtaining the free energy changes of cell reactions. In order to collect the accurate available data in a convenient and useful system, and thus make them part of the general systematization of free energy data, it has been customary to divide cells into two electrode parts, and construct a table of electrode potentials.

Since 1889, when Nernst developed his osmotic theory and his well-known formula for the concentration cell, the importance of obtaining standard electrode potentials has been realized. In 1900, Wilsmore [1] published a table of electrode potentials. In 1911, Abegg, Auerbach and Luther,[2] published a more comprehensive table of similar data. The development up to that time may be regarded as the extensive period. In later years, many electrode potentials have been determined with greater precision. The principal advances during the last ten years have been made with few exceptions by G. N. Lewis and his colleagues. The chief factors leading to these recent developments are the more precise measurements of the activities of electrolytes, the ingenious and accurate method of Lewis and Kraus for obtaining the potentials of the alkali metal electrodes, and the use of metals in a finely divided form as electrodes. These interesting measurements and the calculations of the electrode potentials have been discussed in detail by Lewis and Randall who have also compiled a table of the standard molal electrode potentials at 25°.[3] The present discussion will be confined to the consideration of the necessary conventions, and to the discussion of some methods of calculation.

Conventions and Nomenclature, and Table of Standard Electrode Potentials: [4] According to equation (45), we found that for any chemical reaction a change in free energy referred to a normal state is given by

$$\Delta F - \Delta F_0 = RT \ln \frac{a_{A'_1}^{n'_1} \cdots a_{A'_2}^{n'_2} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots} \cdot \tag{45}$$

By adopting the convention that the electromotive force of the cell is positive when the positive current flows from left to right, we found that a decrease in free energy, $(-\Delta F)$, equals $\mathbf{NEF}$, and, therefore, $(-\Delta F_0)$ equals $\mathbf{NE_0F}$, where $\mathbf{E_0}$ is a standard electromotive force. From these considerations, we obtain

$$\mathbf{E} = \mathbf{E_0} - \frac{RT}{\mathbf{NF}} \ln \frac{a_{A'_1}^{n'_1} \cdots a_{A'_2}^{n'_2} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots} \cdot \tag{141}$$

This equation is true for any cell reaction. Now, we choose as a normal state the condition that the activities equal unity, under which condition $\mathbf{E}$ will equal $\mathbf{E_0}$.

[1] *Z. physik. Chem.*, **35**, 291 (1900).

[2] "Messungen elektromotorische Krafte galvanischer Ketten," Abhandlungen der deutschen Bunsengesellschaft, No. 5. Halle, 1911.

[3] Lewis and Randall, Thermodynamics, McGraw-Hill Book Co. (1923).

[4] Lewis, *J. Am. Chem. Soc.*, **35**, 1 (1913).

Any cell reaction may be broken up into two parts, and the electromotive force of the corresponding cell may be divided into two electrode potentials. For example, the reaction

$$\tfrac{1}{2}Zn + H^+(1M) = \tfrac{1}{2}Zn^{++}(1M) + \tfrac{1}{2}H_2$$

may be split up into

$$(a)\quad \tfrac{1}{2}Zn = \tfrac{1}{2}Zn^{++} + \Theta; \qquad (b)\quad H^+ + \Theta = \tfrac{1}{2}H_2$$

or

$$(a)\quad \tfrac{1}{2}Zn = \tfrac{1}{2}Zn^{++} + \Theta; \qquad (c)\quad \tfrac{1}{2}H_2 = H^+ + \Theta,$$

where Θ represents one Faraday of electrons. The same convention is adopted for the single electrode potentials as for the cells, namely, that its electromotive force is positive when positive current flows from left to right. For the above electrode processes, then, we obtain

$$\left.\begin{aligned} (a)\quad & \mathbf{E} = \mathbf{E}_0 - \frac{RT}{\mathbf{F}} ln a_{Zn^{++}}, \\ (b)\quad & \mathbf{E} = \mathbf{E}_0 - \frac{RT}{\mathbf{F}} ln \frac{p^{1/2}}{a_{H^+}}, \\ (c)\quad & \mathbf{E} = \mathbf{E}_0 - \frac{RT}{\mathbf{F}} ln \frac{a_{H^+}}{p^{1/2}}, \end{aligned}\right\} \qquad (142)$$

where p is the hydrogen pressure.

No method is known for the evaluation of the absolute potential of an electrode, and, for this reason, a standard reference potential must be chosen. It is customary at the present time to refer all electrodes to the hydrogen electrode at one atmosphere pressure in a solution of hydrogen ions of unit activity. Thus, for the hydrogen electrode, $\mathbf{E}_0 = 0$, at all temperatures. By referring all electrodes to the hydrogen electrode, either by direct or indirect comparison, the tables of standard electrode potentials at 25° have been compiled. In Table XXX, Part I, are given the values obtained by Lewis and Randall, taken for the most part from the investigations of Lewis and his associates. References to the original literature are given below the table. The electrode reactions are so arranged that the values for the free energies are equal simply to $(-\mathbf{E}_0\mathbf{F})$. In Part II of the Table are given some values for the electrode potentials of other elements taken from the compilation of Abegg, Auerbach, and Luther. These values are of a far less order of accuracy.

Some Calculations of Standard Electrode Potentials: In order to illustrate the methods of evaluating standard electrode potentials, we shall consider two typical calculations made by Lewis and Randall.

The $Hg|HgCl\ (s)|Cl^-$ *Electrode.* Many measurements of the cell

$$H_2|HCl\ (0.1)|HgCl|Hg$$

by different investigators give 0.3989 for **E**. By equation (141), since the activities of the solid phases are unity,

$$\mathbf{E} = \mathbf{E}_0 - \frac{RT}{\mathbf{F}} ln a_H a_{Cl} = \mathbf{E}_0 - 0.1183 \log c\gamma.$$

TABLE XXX

PART I

Standard Electrode Potentials at 25°

	Electrode	Electrode Reaction	E_0
1.	$Li\|Li^+$	$Li = Li^+ + \Theta$	2.9578
2.	$Rb\|Rb^+$	$Rb = Rb^+ + \Theta$	2.9242
3.	$K\|K^+$	$K = K^+ + \Theta$	2.9221
4.	$Na\|Na^+$	$Na = Na^+ + \Theta$	2.7125
5.	$Zn\|Zn^{++}$	$\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + \Theta$	0.7581
6.	$Fe\|Fe^{++}$	$\frac{1}{2}Fe = \frac{1}{2}Fe^{++} + \Theta$	0.441
7.	$Cd\|Cd^{++}$	$\frac{1}{2}Cd = \frac{1}{2}Cd^{++} + \Theta$	0.3976
8.	$Tl\|Tl^+$	$Tl = Tl^+ + \Theta$	0.3363
9.	$Sn\|Sn^{++}$	$\frac{1}{2}Sn = \frac{1}{2}Sn^{++} + \Theta$	0.136
10.	$Pb\|Pb^{++}$	$\frac{1}{2}Pb = \frac{1}{2}Pb^{++} + \Theta$	0.122
11.	$Fe\|Fe^{+++}$	$\frac{1}{3}Fe = \frac{1}{3}Fe^{+++} + \Theta$	0.045
12.	$Pt\|H_2\|H^+$	$\frac{1}{2}H_2 = H^+ + \Theta$	0
13.	$Cu\|Cu^{++}$	$\frac{1}{2}Cu = \frac{1}{2}Cu^{++} + \Theta$	− 0.3448
14.	$Hg\|Hg_2^{++}$	$Hg = \frac{1}{2}Hg_2^{++} + \Theta$	− 0.7986
15.	$Ag\|Ag^+$	$Ag = Ag^+ + \Theta$	− 0.7995
16.	$Pt\|S^{--}\|S$ (rhomb)	$\frac{1}{2}S^{--} = \frac{1}{2}S$ (rhomb) $+ \Theta$	0.51
17.	$Pt\|OH^-\|O_2$	$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + \Theta$	− 0.3976
18.	$Pt\|I^-\|I_2$ (s)	$I^- = \frac{1}{2}I_2$ (s) $+ \Theta$	− 0.5357
19.	$Pt\|Br^-\|Br$ (l)	$Br^- = \frac{1}{2}Br_2$ (l) $+ \Theta$	− 1.0659
20.	$Pt\|Cl^-\|Cl_2$ (g)	$Cl^- = \frac{1}{2}Cl_2$ (g) $+ \Theta$	− 1.3594
21.	$Hg\|HgCl\|Cl^-$	$Hg + Cl^- = HgCl + \Theta$	− 0.2700
22.	$Ag\|AgCl\|Cl^-$	$Ag + Cl^- = AgCl + \Theta$	− 0.2245
23.	$Hg\|Hg_2SO_4\|SO_4^{--}$	$Hg + \frac{1}{2}SO_4^{--} = \frac{1}{2}Hg_2SO_4 + \Theta$	− 0.6213
24.	$Pt\|H_2\|OH^-$	$\frac{1}{2}H_2 + OH^- = H_2O$ (l) $+ \Theta$	0.8280
25.	$Hg\|HgO\|OH^-$	$\frac{1}{2}Hg + OH^- = \frac{1}{2}HgO + \frac{1}{2}H_2O + \Theta$	− 0.0984

REFERENCES TO PART I, TABLE XXX

(1) (3) Lewis and Keyes, *J. Am. Chem. Soc.*, **34**, 119 (1912); **35**, 340 (1913).
(2) Lewis and Argo, *ibid.*, **37**, 1983 (1915).
(4) Lewis and Kraus, *ibid.*, **32**, 1459 (1910).
(5) (7) Horsch, *ibid.*, **41**, 1787 (1919).
(8) Lewis and von Ende, *ibid.*, **32**, 732 (1910).
(9) Noyes and Toabe, *ibid.*, **39**, 1537 (1917).
(13) (23) Lewis and Lacy, *ibid.*, **36**, 804 (1914).
(14) Linhart, *ibid.*, **38**, 2356 (1916).
(15) Noyes and Braun, *ibid.*, **34**, 1016 (1912).
(16) Sammet, *Z. physik. Chem.*, **53**, 641 (1905); Maitland, *Z. Elektrochem.*, **12**, 263 (1906).
(19) Lewis and Storch, *J. Am. Chem. Soc.*, **39**, 2544 (1917).
(20) Lewis and Rupert, *ibid.*, **33**, 299 (1911).
(21) Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).
(23) Randall and Cushman, *ibid.*, **40**, 393 (1918).
(24) Lorenz and Bohi, *Z. physik. Chem.*, **66**, 733 (1909).
(25) Brönsted, *Z. physik. Chem.*, **65**, 84 (1909); **65**, 744 (1909). Ming Chow, *J. Am. Chem. Soc.*, **42**, 488 (1920).

PART II

Electrode	Electrode Reaction	E_0
1. $Ba\|Ba^{++}$	$\frac{1}{2}Ba = \frac{1}{2}Ba^{++} + 0$	2.8
2. $Sr\|Sr^{++}$	$\frac{1}{2}Sr = \frac{1}{2}Sr^{++} + 0$	2.7
3. $Ca\|Ca^{++}$	$\frac{1}{2}Ca = \frac{1}{2}Ca^{++} + 0$	2.5
4. $Mg\|Mg^{++}$	$\frac{1}{2}Mg = \frac{1}{2}Mg^{++} + 0$	1.55
5. $Mn\|Mn^{++}$	$\frac{1}{2}Mn = \frac{1}{2}Mn^{++} + 0$	1.0
6. $Cr\|Cr^{+++}$	$\frac{1}{3}Cr = \frac{1}{3}Cr^{+++} + 0$	0.5
7. $In\|In^{+++}$	$\frac{1}{3}In = \frac{1}{3}In^{+++} + 0$	0.35
8. $Co\|Co^{++}$	$\frac{1}{2}Co = \frac{1}{2}Co^{++} + 0$	0 29
9. $Ni\|Ni^{++}$	$\frac{1}{2}Ni = \frac{1}{2}Ni^{++} + 0$	0.22
10. $Sb\|Sb^{+++}$	$\frac{1}{3}Sb = \frac{1}{3}Sb^{+++} + 0$	− 0.1
11. $Bi\|Bi^{+++}$	$\frac{1}{3}Bi = \frac{1}{3}Bi^{+++} + 0$	− 0.2
12. $As\|As^{+++}$	$\frac{1}{3}As = \frac{1}{3}As^{+++} + 0$	− 0.3
13. $Pd\|Pd^{++}$	$\frac{1}{2}Pd = \frac{1}{2}Pd^{++} + 0$	− 0.82
14. $Au\|Au^{+}$	$Au = Au^{+} + 0$	− 1.5
15. $Pt\|F^{-}\|F_2$	$F^{-} = \frac{1}{2}F_2 + 0$	− 1.9

Lewis and Randall take the activity coefficient of the acid to be 0.811 at 0.1 molal. Using this value, E_0 equals 0.2700, which is the electromotive force of the cell when both a_H and a_{Cl} equal unity, or the standard electromotive force of the cell. If the cell is divided into

$$(a)\quad Pt|H_2|H^{+} \qquad \text{and} \qquad (b)\quad Hg|HgCl|Cl^{-},$$

then it is obvious that $0.2700 = E\,(a) - E\,(b)$, and since $E\,(a) = 0$,

$$Hg|HgCl|Cl^{-}; \qquad E_0 = -0.2700.$$

From this value, the electromotive force of the electrode $Hg|HgCl|KCl$ (0.1) may be computed by the equation

$$E = E_0 - \frac{RT}{F} ln \frac{1}{a_{Cl}}.$$

Lewis and Randall take 0 0794 as the activity of the chloride ion ($\sqrt{a_K a_{Cl}}$) in 0.1 molal potassium chloride, and obtain

$$Hg|HgCl|KCl\ (0.1); \qquad E = -0.3351.$$

The Sodium Electrode. Lewis and Kraus measured the cell

$$Na\ (s)|NaI\ in\ C_2H_5NH_2|0\ 206\ per\ cent\ Na\text{-}amalgam$$

and obtained 0.8453 for its electromotive force. They found that the sodium electrode under these conditions was far more reproducible than any other metal electrode. Consequently,

$$Na\ (s)|Na\ (0.206\ per\ cent\ amalgam); \qquad E = 0.8453.$$

In their investigation, Lewis and Kraus employed cells with liquid junctions. Lewis and Randall, in a more recent calculation, have shown that these liquid junctions may be avoided. Thus, from the results of Allmand and Polack,[1] Lewis and Randall obtained by interpolation

$$Na\ (0.206\ per\ cent\ amalgam)|NaCl\ (1.022)|HgCl|Hg; \qquad E = 2.1582$$

and, therefore, by combination

$$Na\ (s)|NaCl\ (1.022)|HgCl|Hg; \qquad E = 3.0035$$

[1] *J. Chem. Soc.*, **115**, 1020 (1919).

The activity coefficient of 1.022 molal sodium chloride is taken to be 0.650, whence

$$Na\ (s)\,|\,Na^+\ (1)\,||\,Cl^-\ (1)\,|\,HgCl\,|\,Hg; \qquad E_0 = 2.9825.$$

It has already been found that the electromotive force of the standard calomel electrode is − 0.2700, and, consequently,

$$Na\ (s)\,|\,Na^+; \qquad E_0 = 2.7125.$$

This ingenious method, which has more recently been applied in determining the other alkali metal electrodes, constitutes the most important advance made in the last decade in the determination of standard electrode potentials.

Electrode Potentials and Equilibrium Constant: From equation (45) it follows that at equilibrium, since $\Delta F = 0$,

$$\Delta F_0 = -RT ln K,$$

where K is the equilibrium constant, and, therefore,

$$E_0 = \frac{RT}{NF} ln K = \frac{0.05915}{N} \log K. \tag{143}$$

This important equation permits the direct evaluation of the equilibrium constant of a reaction from the table of standard electrode potentials.

(*a*) *The Ionic Product of Water at 25° C.:* From Table XXX we find that

$$\tfrac{1}{2}H_2 = H^+ + 0; \qquad E_0 = 0$$

and

$$\tfrac{1}{2}H_2 + OH^- = H_2O\ (l) + 0; \qquad E_0 = 0.8280.$$

Subtracting the second of these equations from the first, we obtain

$$H_2O\ (l) = H^+ + OH^-; \qquad E_0 = -0.8280$$

and, by equation (113), since the liquid has unit activity,

$$-0.8280 = 0.05915 \log a_H a_{OH} = 0.05915 \log K_w,$$

whence

$$K_w = 1.005 \times 10^{-14}$$

at 25°.

(*b*) *Solubility Product.* From the Table we find that

$$Ag + Cl^- = AgCl + 0; \qquad E_0 = -0.2245$$

and

$$Ag = Ag^+ + 0; \qquad E_0 = -0.7995,$$

whence

$$Ag^+ + Cl^- = AgCl, \qquad E_0 = 0.5750.$$

By equation (113), we obtain

$$0.5750 = 0.05915 \log \frac{1}{a_{Ag} a_{Cl}} = 0.05915 \log \frac{1}{S}$$

from which

$$S = 1.90 \times 10^{-10}$$

at 25°.

(c) *Replacement Equilibrium:* From reactions (5) and (12) in Table XXX, we find that

$$\tfrac{1}{2}Zn + H^+ = \tfrac{1}{2}H_2 + \tfrac{1}{2}Zn^{++}; \qquad E_0 = 0.7581$$

and by equation (143)

$$0.7581 = 0.05915 \log K = 0.05915 \log \frac{a_{Zn^{++}}^{1/2} p_{H_2}^{1/2}}{a_H}$$

from which we find that

$$K = 6.45 \times 10^{12}.$$

If we had a solution containing zinc and hydrogen ions at unit activity, and immersed in it a strip of pure zinc, it may be calculated from this value of the equilibrium constant that a pressure of 2.53×10^{25} atmospheres would be required to prevent the formation of hydrogen.

Effect of Pressure on Electromotive Force: The pressure coefficient of free energy of a system at constant composition and at constant temperature has been shown to be in general

$$\left[\frac{\partial F}{\partial p}\right]_{N,\,T} = V,$$

where V is the volume of the system. For a variation of an increment in free energy of a process, we obtain

$$\left[\frac{\partial \Delta F}{\partial p}\right]_{N,\,T} = \Delta V, \tag{144}$$

where ΔV is the volume change of the process. In an electrode or a cell process involving the passage of one Faraday, $\Delta F = -\mathbf{EF}$, and, therefore,

$$\left[\frac{\partial \mathbf{E}}{\partial p}\right]_{T,\,N} = -\frac{\Delta V}{\mathbf{F}}. \tag{145}$$

Let us now apply this equation to the cell

$$H_2 \,|\, HCl\ (0.1M) \,|\, HgCl \,|\, Hg,$$

which possesses a gas electrode, subject to large changes in volume. The cell reaction, corresponding to the passage of one Faraday, is

$$\tfrac{1}{2}H_2 + HgCl = HCl\ (0.1) + Hg$$

and the total change in volume is

$$\Delta V = (\overline{V}_{HCl} + V_{Hg}) - (\tfrac{1}{2}V_{H_2} + V_{HgCl}). \tag{146}$$

For small pressures, and small changes in pressure, $\frac{1}{2}V_{H_2} = \frac{1}{2}\dfrac{RT}{p}$, and, if we neglect the volume changes of the solids and solutions which are small compared to that of the gas,

$$\partial \mathbf{E} = \frac{RT}{2\mathbf{F}}\,\partial ln p \tag{147}$$

is obtained by means of equation (145). The change in electromotive force,

$\Delta\mathbf{E}$, produced by a change in pressure from one atmosphere to p atmospheres is

$$\Delta\mathbf{E} = \int_1^p \frac{RT}{2\mathbf{F}}\,\partial \ln p = \frac{RT}{2\mathbf{F}}\ln p. \qquad (148)$$

$\Delta\mathbf{E}$ at low pressures is really the change in electromotive force at the hydrogen electrode. If the process at the hydrogen electrode is reversible, then $\mathbf{E}$ should vary with the hydrogen pressure, p, according to this equation. Measurements of this variation with pressure afford a simple means of testing the reversibility of hydrogen or other gas electrodes. Lewis and Randall,[1] Ellis,[2] and Loomis and Acree [3] have found that for small changes of pressure this equation is valid. Equation (148) has been employed for correcting electromotive forces of cells with a hydrogen electrode to one atmosphere hydrogen pressure.

More recently, Hainsworth and MacInnes [4] have measured the electromotive force of the hydrogen-calomel cell at different pressures up to 400 atmospheres. They employed the equation of state of Keyes [5] for the hydrogen pressure, and took into consideration the factors involving the changes in $\overline{V}_{HCl}$, V_{Hg} and V_{HgCl} with the pressure. Their calculated results agreed very closely with the observed results up to 50 atmospheres hydrogen pressure, above which a slight uniform deviation appeared, which they attributed to the solubility of hydrogen.

The effect of high pressures on the electromotive forces of many cells not containing gas electrodes forms an important part of the "Piezochemical Studies" of Cohen and his colleagues [6]

Some General Considerations: A glance at the table of standard electrode potentials which represents the best results of many investigators during the last thirty years will show that it is far from being very comprehensive. Apart from the determination of the standard electrode potentials, there remains the study of the variation of the electrode potentials with the concentration, the pressure and the temperature. The recent accurate studies of concentration cells, freezing point lowerings, etc., have furnished the data of the type necessary for computing the variation with the concentration. This work has been discussed in detail. The temperature variations of both activities and electrode potentials constitute a very important field for investigation. Although the methods are well known, there are not sufficient accurate data available to warrant a systematization. Further development awaits data on partial specific heats, and heat contents of the ions and their variations with the temperature; the electromotive forces, the heat content changes of cell reactions and their variations with the temperature Such data will lead to a more and more complete knowledge of reversible processes involving solutions, of cell reaction equilibria, and the inner equilibria in solutions. On such a firm foundation, we may then proceed with greater security to the more inexact, difficult, and conjectural fields of electrochemistry which involve irreversible processes.

[1] *J. Am. Chem. Soc.*, **36**, 1969 (1914).
[2] *J. Am. Chem. Soc.*, **38**, 737 (1916).
[3] *J. Am. Chem. Soc.*, **38**, 2391 (1916).
[4] *J. Am. Chem. Soc.*, **44**, 1021 (1922), **46**, 1437 (1924).
[5] *Proc. Nat. Acad. Sci.*, **3**, 323 (1917); *J. Am. Chem. Soc.*, **46**, 589 (1919).
[6] These contributions occur in *Z. physik. Chem.* from 1909 to the present time. We may cite "Piezochemische Studien XX," Cohen, Ishikawa, and Moesveld, *Z. physik. Chem.*, **105**, 155 (1923).

Theories of Electrode Processes

Thermodynamics alone yields no knowledge regarding the inner constitution of a system. In order to apply thermodynamic equations to a system, it is necessary to have an equation of state for that system, and, if such an equation is to be other than purely empirical, it must rest on a knowledge or hypotheses regarding the inner constitution of the system. Nor does thermodynamics give the desired information regarding the inner mechanism of reactions, or the nature of processes occurring at electrodes. It will be of interest now to consider briefly some theories outside the domain of exact thermodynamics which have been employed to account partially for the production of galvanic electricity and the mechanism of electrode processes.

Standard Electrode Potentials of the Elements and Atomic Numbers: That the standard molal electrode potential is a fundamental property of an element becomes evident upon inspection of Fig. 13, wherein the values of the electrode potentials of the elements given in Table XXX are plotted against the atomic numbers. Well-marked periodicity is observable. The result is

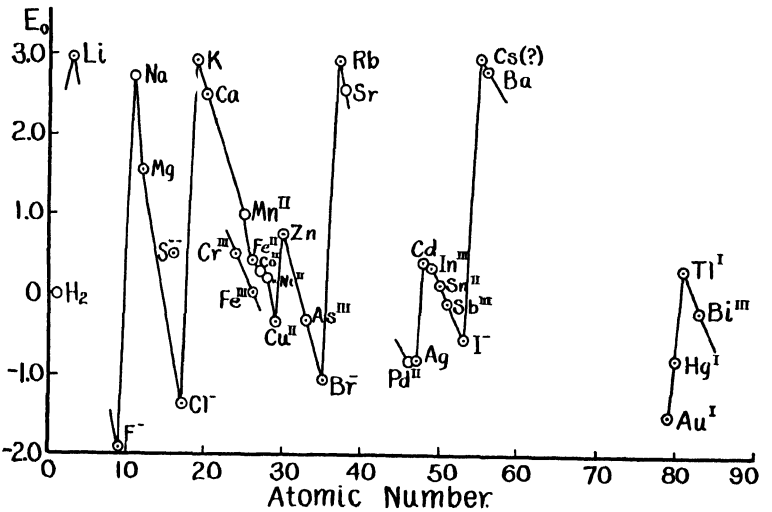


Fig. 13. Molal Electrode Potentials

approximate owing to the many variables involved, and to the somewhat arbitrary manner in which unit activity of the electrolytes has been defined.

In Table XXX, the electrode reactions have been written as a reaction involving the formation of electrons. Since the free energy decrease of the reaction: $Li = Li^+ + \Theta$ is greater than that of the reaction: $Ag = Ag^+ + \Theta$, we may say that lithium has a greater tendency to form ions and electrons than silver.[1] Similarly, the bromide ion has a greater tendency to form

[1] It must be borne in mind in the present discussion that the ions are in aqueous solution and at unit activity.

electrons and the element than the chloride ion. In plotting these results, elements which form cations have been compared to the anions, and not to the elements which form anions. That is to say, all electrode processes are taken in the direction of electron formation. Considered in this way, the halogen and sulphide ion electrode potentials fall into well-defined positions. Viewed from the standpoint of atomic theory, we are in this way comparing the tendency of electron shells to give off electrons.

The more electropositive the element, the greater its tendency to form ions and electrons. The more electronegative the element, the greater its tendency to react with an electron to form the anion. If these simple equations represent the true electrode processes, then the electrode potentials are a relative measure of the free energy decrease or affinity of these reactions. This idea was embodied in the theory of "electro-affinity" of Abegg and Bodländer.[1]

The Electrical Double Layer and Osmotic Theory: From the preceding considerations, it appears that all metals have a tendency to go into solution to form cations. Nernst [2] regarded such a tendency as being caused by the "electrolytic solution pressure" of the metal. When a metal such as zinc is immersed in water or in a solution of a salt, its electrolytic solution pressure, which may be very high, tends to form ions of the metal in the solution. In so doing it carries positive charges into the solution which becomes positively charged, and, consequently, leaves the metal negatively charged. This electrical double layer of negative charges on the metal surface and positive charges in the solution near the metal sets up an electrostatic field of great intensity which retards further passage of the metal into the solution. This layer is regarded as being the underlying cause of contact differences of potential at such surfaces.[3]

When a metal is immersed in a solution containing its ions, the factors which determine the electromotive force at the boundary are, according to Nernst, the electrolytic solution pressure of the metal and the osmotic pressure of the metallic ions. Thus, if the solution pressure is greater than the osmotic pressure, the electrode will be charged negatively to the solution, and, vice versa, if the osmotic pressure of the ion is greater than the solution pressure of the metal. From these postulates, Nernst showed that the electrode potential of a metal would be given by the equation

$$\mathbf{E} = \frac{RT}{\mathbf{NF}} ln \frac{P}{\pi},$$

where P is the solution pressure of the metal and π is the osmotic pressure of its ions.

[1] *Z. anorg. Chem.*, **20**, 453 (1899).

[2] *Z. physik. Chem.*, **4**, 150 (1889).

[3] The electrical double layer theory had been employed by Lippmann (*Pogg. Ann.*, **149**, 547 (1873); *Wied. Ann.*, **11**, 316 (1880), and by Helmholtz (Helmholtz, Ges. Abh., **1**, 925) in order to explain capillary electrical phenomena.

Smits' Theory of Electrode Equilibrium: The net effect of an electrode reaction of a metal is given by the reaction:

$$Me = Me^{\nu+} + \nu\Theta.$$

This represents a process but gives no insight into the nature of the state of the system when the metal is in equilibrium with a solution of its ions. In accord with the theory of Nernst, it has usually been supposed that the heterogeneous equilibrium between the metal and the solution would be represented by the simple equation

$$Me_s \rightleftharpoons Me_l^{\nu+} + \nu\Theta,$$

where $Me_l^{\nu+}$ is in the solution phase, and Me_s is the solid metal. The true nature of the state of such an equilibrium is at present a matter of speculation.

As a part of the development of his theory of allotropy, Smits[1] has proposed a theory of electromotive force of metal-solution boundaries, which, although highly conjectural, is of particular interest when irreversible electromotive forces are considered. In general, the fundamental proposition of Smits' theory is that all phases, even a phase of one component, such as orthorhombic sulphur, or red phosphorus, is itself complex, or composed of two or more "pseudo-components" which may be molecules, ions, electrons, etc. These pseudo-components may or may not be in stable equilibrium in the phase. The behavior of the phase will depend on its inner equilibrium, and the extent to which this inner equilibrium may be displaced. This idea will become clear when we consider its application to the supposed inner equilibrium which exists between a metal and a solution containing ions of the metal.

The choice of the pseudo-components of a metal phase is somewhat arbitrary. Of the many possible kinds of inner equilibria of the solid metal phase, we may select

$$Me_s \rightleftharpoons Me_s^{\nu+} + \nu\Theta,$$

where the pseudo-components are metal molecules or atoms, metallic ions, and electrons. The subscript "s" refers to the solid state, and, consequently, the above equation represents a homogeneous reaction. When the metal is brought into contact with the solution, all of these pseudo-components are assumed to exist in the solution, and an equilibrium will be established between the two phases which will be represented by

$$\begin{array}{ccccc} Me_s & \rightleftharpoons & Me_s^{\nu+} + \nu\Theta_s, \\ \Updownarrow & & \Updownarrow \quad \Updownarrow \\ Me_l & \rightleftharpoons & Me_l^{\nu+} + \nu\Theta_l, \end{array}$$

where the symbols with the subscript l refer to the solution. Such an equilibrium requires the equality of the partial free energies, or activities of each pseudo-component in the solid and liquid phases. Smits has employed this equation to represent the electrode equilibrium, and, on this basis, has developed mathematical equations for reversible electrode potentials, concentration cells, etc. Some metals may have a greater phase complexity than above represented. For example, the pseudo-components of iron may be Fe^{++}, Fe^{+++}, Fe, and Θ.

When stable equilibrium exists between the pseudo-components in the metal, in the solution, and between the metal and the solution, the electrode will be reversible and its potential will have its corresponding value. If, on the other hand, the inner equilibrium of the system be disturbed by electrolysis, or by some chemical means, the potential may vary far from its normal value. This will also be the case if the inner equilibrium of the metal

[1] Smits, Versl. Kon. Akad. v. Wet., **22**, 642 (1913); **27**, 1 (1918); **27**, 981 (1919); **27**, 1470 (1919).

Smits and Aten, *Z. physik. Chem.*, **90**, 723 (1915); **92**, 1 (1916).

Smits and Byvoet, Versl. Kon. Akad. v. Wet., **27**, 311 (1918).

For a complete development of the theory, see Smits, *The Theory of Allotropy*. English Translation. Longmans, Green & Co. (1922).

surface be displaced. On removing the disturbing cause, the potential will return to its normal value as inner equilibrium is again established. This latter process may take place with different degrees of rapidity and may depend on the presence of positive and negative catalysts.

INTRODUCTION TO ELECTROLYSIS AND POLARIZATION PHENOMENA

Imagine the electromotive force of a galvanic cell to be exactly balanced at a given instant by a constant external electromotive force. The cell will be reversible if every substance composing it is in a stable state, and if a very small increase in the applied external electromotive force will cause reactions which will be exactly reversed by a very small decrease in the external electromotive force. As long as these conditions prevail, the electromotive force of the cell will remain constant, and will correspond to the free energy decrease of the cell reaction.

If, on the contrary, any actual process brought about by chemical reaction or by electrolysis is taking place in the cell, the system will be undergoing an irreversible change and its electromotive force will vary with the time. In the following discussion, such irreversible changes produced at electrodes by electrolysis will be considered.

Electrolysis and Reversible Electrode Potentials, Counter Electromotive Force, Decomposition Potential, Polarization, and Overvoltage: Let **E** represent the electromotive force of the cell

$$\mathrm{Pt}\,|\,\mathrm{H_2}\ (1\ \mathrm{atm.})\,|\,\mathrm{HCl}\ (c)\,|\,\mathrm{Cl_2}\ (1\ \mathrm{atm.})\,|\,\mathrm{Pt}$$

of which the cell reaction is

$$\tfrac{1}{2}\mathrm{H_2} + \tfrac{1}{2}\mathrm{Cl_2} = \mathrm{HCl}\ (c).$$

E is measured by balancing as nearly as possible with an opposing external electromotive force, whereby only a very small current passes in either direction through the cell. The reverse of the above reaction represents the electrolysis of the solution, from which it at once becomes apparent that in order to electrolyze the solution between platinum electrodes, an electromotive force, e, greater than **E** must be applied. Under these conditions, **E** is a counter electromotive force, and is equal to the decomposition potential of the electrolyte, or the minimum electromotive force which must be applied in order to produce electrolysis.

During electrolysis, then, according to Ohm's law, we have

$$e - \mathbf{E} = CR, \tag{1}$$

where C is the current and R the resistance of the system. If e is only very slightly greater than **E**, the current density, or the current per unit of electrode area, will be very small and **E** will very nearly equal the reversible electromotive force of the cell. When e is considerably greater than **E**, and, consequently, the current density higher, considerable electrolysis will take place, which will produce physical and chemical changes in the system, and cause **E** to vary from

its reversible value. Under these conditions, the cell and the cell electrodes are said to have undergone polarization. In general, polarization is any change produced at an electrode by electrolysis or by some other means which causes its potential to differ from its reversible or normal value.

The difference between the potential of an electrode which has undergone polarization and its reversible electrode potential in a solution of the same concentration of electrolyte we shall denote as the "overvoltage" of the electrode. Thus, the overvoltage of the hydrogen electrode in the above cell would equal the electromotive force of the irreversible cell

$$\mathrm{Pt}\,|\,\mathrm{H_2}\ (\text{depositing})\,|\,\mathrm{HCl}\ (c)\,|\,\mathrm{H_2}\ (\text{reversible})\,|\,\mathrm{Pt}.$$

Concentration Polarization: In all measurements of the electromotive force of reversible cells, so little current is allowed to flow that any concentration changes in the neighborhood of the electrodes are negligible. If, on the other hand, a considerable flow of electricity takes place either by discharging or charging the cell, concentration changes will take place in the neighborhood of the electrodes which may considerably alter the electromotive force of the cell. If the electrolyte is not stirred, these concentration changes can only be adjusted by the slow process of diffusion of the electrolyte.

At the beginning of the electrolysis of a copper sulphate solution between copper electrodes, the counter electromotive force is zero since the electrode potentials of the anode and cathode are equal. In order to electrolyze the solution, the applied electromotive force would only have to be sufficient to overcome the resistance of the solution. During electrolysis the copper ion concentration at the anode and at the cathode will increase and decrease, respectively. The net effect will be the production of a counter electromotive force equal to that of the concentration cell produced by the electrolysis. This counter electromotive force will be greater the greater the current density; it can be much reduced or eliminated by stirring.

When charged, the lead accumulator is

$$\mathrm{Pb}\,|\,\mathrm{PbO_2}\,|\,\mathrm{H_2SO_4}\ (c)\,|\,\mathrm{Pb}$$

and when completely discharged it is

$$\mathrm{Pb}\,|\,\mathrm{PbSO_4}\,|\,\mathrm{H_2SO_4}\ (c')\,|\,\mathrm{PbSO_4}\,|\,\mathrm{Pb}.$$

The cell reaction [1] has usually been thought to be

$$\mathrm{Pb} + \mathrm{PbO_2} + 2\mathrm{H_2SO_4}\ (c) = 2\mathrm{PbSO_4} + 2\mathrm{H_2O}.$$

A lead accumulator containing 20.9 per cent sulphuric acid has a normal electromotive force of 2.010 volts at 15°. On charging the partially discharged cell, its electromotive force rapidly rises to 2.1 volts, then more slowly to 2.2, and then rapidly to 2.6. If the cell is then allowed to stand without charging,

[1] That this may not be the correct cell reaction has been suggested by Fery, *J. Phys.*, **6**, 21 (1916). See also MacInnes, Adler, and Joubert, *Trans. Am. Electrochem. Soc.*, **37**, 641 (1920).

its electromotive force soon changes to its normal value. During discharging, the electromotive force drops rapidly to 1.9, then slowly to 1.8 volts, and finally decreases more rapidly. If left undisturbed, the electromotive force rapidly rises to its normal value of 2.01 volts. These observations are due to Dolezalek[1] who has made a very comprehensive study of this cell. These variations of the electromotive force from its normal value are supposed to be almost if not entirely caused by concentration polarization. Sulphuric acid accumulates at both electrodes during charging and the process of diffusion is retarded by the porous lead dioxide.

Decomposition Potentials at Low Current Densities: In general, when a solution is placed between two platinum electrodes and an external voltage applied, a small current is first produced which drops and remains almost at zero until the decomposition potential is reached, and then, if the applied electromotive force be increased further, electrolysis will take place and the current will thereafter increase proportionally to the applied electromotive force. Under these conditions, the decomposition potential is equal to the counter electromotive force of the reversible or irreversible cell made up of the solution, the electrodes, and the products of the initial electrolysis.

Decomposition potentials may be measured by determining the break in the curve obtained by plotting the applied electromotive force against the current, or electrolyzing the solution by a definite external potential until the electrodes are charged with the decomposition products of electrolysis, interrupting this circuit, and then short circuiting the electrodes through a high resistance circuit containing a voltmeter or a high resistance potentiometer.

The principal investigations of decomposition potentials of acids, bases, and salts, in aqueous solutions, between platinum electrodes, and at low current densities, were made by Le Blanc.[2] Table XXXI contains some of the values for normal salt solutions.

TABLE XXXI

DECOMPOSITION POTENTIALS OF NORMAL SALT SOLUTIONS

Electrolyte	Decomposition Potential (volts)	Electrolyte	Decomposition Potential (volts)
$ZnSO_4$	2.35	$NiCl_2$	1.85
$NiSO_4$	2.09	$ZnBr_2$	1.80
$CdSO_4$	2.03	$CoCl_2$	1.78
$Cd(NO_3)_2$	1.98	$Pb(NO_3)_2$	1.52
$CoSO_4$	1.92	$AgNO_3$	0.70
$CdCl_2$	1.88		

At the cathode, the counter electromotive force will be produced by the boundary of the deposited metal and its ions, and will correspond to the reac-

[1] Theory of the Lead Accumulator. English Translation by von Ende. Wiley & Sons, (1910).

[2] *Z. physik. Chem.*, 8, 299 (1891); Text-book of Electrochemistry, Le Blanc. English Translation by Whitney and Brown.

tion, $Me = Me^{\nu+} + \nu\Theta$. The anode reactions are more complicated and obscure. At very low current densities, if the metal is deposited in a stable condition, the counter electromotive force at the cathode should equal the reversible electrode potential of the metal. Under these ideal conditions, the decomposition potential is a minimum. That this is roughly the case for the above experimental results may be seen from the following examples. The difference between the decomposition potentials of zinc and cadmium sulphate is 0.32 volt while the difference between the molal electrode potentials of zinc and cadmium is 0.36 volt; and the difference between the decomposition potentials of cadmium and silver nitrates is 1.28 volts while the difference between the molal electrode potentials of cadmium and silver is 1.20 volts.

The decomposition potentials between platinum electrodes of some acids and bases as determined by Le Blanc are given in Table XXXII.

TABLE XXXII

NORMAL DECOMPOSITION POTENTIALS OF ACIDS AND BASES

Electrolyte	Decomposition Potential (volts)	Electrolyte	Decomposition Potential (volts)
H_2SO_4	1.67	HCl	1.31
HNO_3	1.69	HI	0.52
H_3PO_4	1.70	NaOH	1.69
$CH_2ClCOOH$	1.72	NH_4OH	1.74
$HClO_4$	1.65	$N(C_2H_5)_4OH$ (0.125M)	1.74

There is much less variation in the decomposition potentials of most acids and bases than in those of the salts. Most of the values were found to be between 1.65 and 1.75 volts. Le Blanc pointed out that those acids and bases with a decomposition potential in the neighborhood of 1.70 volts deposited hydrogen and oxygen at the electrodes, and that 1.70 volts equalled approximately the decomposition potential of water on platinum electrodes. The potential of the reversible oxygen-hydrogen cell is about 1.2 volts. The difference between this and 1.7 volts is caused by polarization effects. The decomposition potentials of normal hydrochloric and hydriodic acids are nearly equal to the electromotive forces of the reversible cells

$$Pt \mid H_2 \mid HCl\ (M) \mid Cl_2 \mid Pt$$

and

$$Pt \mid H_2 \mid HI\ (M) \mid I\ (s) \mid Pt,$$

which are 1.36 and 0.53 volts, respectively. In normal solutions of these acids, therefore, chlorine and iodine are deposited. Le Blanc found that if the hydrochloric acid solution be diluted, its decomposition potential will increase, and hydrogen and oxygen will be evolved. Thus, a 0.03N hydrochloric acid solution was found to have a decomposition potential of 1.69 volts.

Cathode Potentials during Metal Deposition: The magnitude of the variation of the electrode potentials of metals with a change in current density differs considerably with the different metals. In Table XXXIII are given some values of the cathode potentials at round current densities, read off plots of the results of Foerster and his collaborators.[1] These potentials are referred

[1] Foerster, Abh. Deutsch. Bunsengesellschaft. No. 2 (1909); Schweitzer, *Z. Elektrochem.*, 15. 602 (1909).

to the normal hydrogen electrode, and were determined at 20°. All the salt solutions were normal. The copper sulphate solution contained 0.01 normal sulphuric acid, and the other salt solutions contained 0.5 per cent of boric acid.

TABLE XXXIII

CATHODE POTENTIALS OF METALS AT DIFFERENT CURRENT DENSITIES

Current Density $\left(\frac{10^{-4}\text{ amperes}}{\text{Cm.}^2}\right)$	Cathode Potentials			
	$CuSO_4$	$FeSO_4$	$NiSO_4$	$CoCl_2$
0	− 0.303	0.465	(0.220)	0.290
1	− 0.294	0.580	0.445	0.370
5	− 0.285	0.619	0.524	0.415
10	− 0.275	0.630	0.546	0.430
20	− 0.270	0.645	0.559	0.440
40	− 0.260	—	0.570	0.459
80	− 0.240	—	0.590	0.495

The variation of the electrode potential of copper is very much less than that of the metals of the iron group. Further confirmation of this point is found in some more recent determinations of metal overvoltage. According to the definition, the metal overvoltage during metal deposition will equal the electromotive force of the cell

$$\text{Me (depositing)} \mid \text{Me}^{\nu+} \mid \text{Me (reversible)}$$

Newbery,[1] by employing an intermittent, instead of a direct, current, obtained 0.02, 0.00, 0.02, 0.00, 0.01, 0.02, 0.82, 0.30, 0.46, for the overvoltages of copper, silver, zinc, lead, cadmium, thallium, nickel, iron, and cobalt, respectively, at a current density of 100 milliamperes per sq. cm.

One plausible explanation of this behavior, employed by Foerster, is that the electrode process, $\frac{1}{2}\text{Me}^{\nu+} + \nu\Theta \rightarrow \frac{1}{2}\text{Me}$, proceeds more slowly in the cases where there is a high degree of polarization. Such a retardation would set up a potential opposite in direction to the external electromotive force, and, consequently, a higher applied electromotive force would be required in order to produce the same current density.

Much more pronounced polarization effects are observed when a metal is deposited from a solution of a complex compound than from a solution of a simple salt. A solution containing a complex ion such as $Cu(CN)_2^{-}$ [2] would contain few Cu^+, and these would be removed almost immediately by electrolysis. The electrode potential might then depend on the rate at which the complex ion decomposed into the metal ion. The slower this velocity, the greater would be the polarization, and the more pronounced the observed change in cathode potential.

[1] Mem. Proc. Manchester Lit. Phil. Soc. 61, Parts II and III, Mem. No. 9 (1917).

[2] Spitzer, *Z. Elektrochem.*, 11, 345 (1905).

Nature of Metallic Deposits: The physical state of electrolytically deposited metals varies widely with the nature of the electrolyte, the current density, and other factors. By varying the conditions of electrolysis, the same metal may be deposited in a crystalline form or in the condition of a spongy mass. The difference of potential between two electrodes of the same metal in such different physical states in a solution of a salt of the metal may be as high as a few tenths of a volt.

That this is true has been shown by numerous investigators. Lewis and his associates have shown that the most reproducible metal electrodes are those of the alkali metals. Lewis and Brighton [1] found that sticks of lead six years old had the same potential as a lead tree freshly precipitated by electrolysis. Lewis and Lacey [2] found that finely divided electrolytically precipitated copper gave reproducible results. On the other hand, the potential of iron in different states of division differed very considerably.[3] Reproducibility of the iron potential may be obtained by employing a finely divided metal. Similar phenomena have been observed in the case of the nickel electrode.[4] Lewis and Brighton conclude "that the lack of reproducibility in electrodes of solid metal is due solely to conditions of strain in the solid surface. In the case of metals which flow readily, like lead, or sodium, or potassium, these accidental strains almost immediately disappear and the solid metals form entirely reproducible electrodes."

If a metal is deposited in a highly strained condition, it will tend to change into a more stable form, or tend to contract. This phenomenon is therefore closely associated with the peeling of electrolytically deposited metals. That there is a tendency for such deposits to contract has been strikingly shown by Kohlschütter and Vuilleumier,[5] and Vuilleumier,[6] who measured the degree of contraction of electrolytically deposited metals by means of a contractometer devised by them. This instrument consists of a thin platinum foil cathode to which is attached a glass pointer 30 cms. in length. The metal is deposited on one side of the foil, and, when contraction of the metal takes place, the foil is bent, and the movement of the point read off the scale. Definite contraction of the metals was observed. The contraction effect was relatively small for copper and silver, and large for nickel and iron. These facts are in agreement with the conclusion of Lewis and Brighton, according to which very little contraction would be observed in the cases of electrolytically deposited soft metals such as lead, sodium, or potassium.

Overvoltage of Hydrogen: In accord with previous considerations, we may define the overvoltage of hydrogen as the difference of potential between a reversible hydrogen electrode and an electrode in the same solution upon which

[1] *J. Am. Chem. Soc.*, **39**, 1906 (1917).

[2] *J. Am. Chem. Soc.*, **36**, 804 (1914).

[3] Richards and Behr, *Z. physik. Chem.*, **58**, 301 (1907).

[4] Euler, *Z. anorg. Chem.*, **41**, 93 (1904); Schoch, *Am. Chem. J.*, **41**, 208 (1909); Schweitzer, *Z. Elektrochem.*, **15**, 607 (1909).

[5] *Z. Elektrochem.*, **24**, 300 (1918).

[6] *Trans. Am. Electrochem. Soc.*, **42**, 99 (1922).

hydrogen is being deposited from hydrogen ions. The overvoltage will equal the electromotive force of the cell

$$\text{Me } (H_2 \text{ depositing}) \,|\, H_2SO_4 \quad \text{or} \quad \text{NaOH, etc.} \,|\, H_2 \text{ (reversible)} \,|\, \text{Pt}$$

and will be positive.

There has been considerable controversy recently in regard to the correct method of measuring hydrogen overvoltage. In the earlier work of Caspari,[1] Tafel,[2] Müller,[3] and others, the overvoltage was measured while a continuous current electrolysis was taking place. Newbery,[4] who has made the most extensive investigation of overvoltage, has employed a rotating commutator by means of which the applied voltage circuit as well as the reference electrode circuit breaks and makes about 2,500 times a minute. Results obtained by the commutator and intermittent current are invariably lower than those obtained by the continuous current method. That this is the case may be seen from the results in Table XXXIV, taken from a recent investigation of Glasstone.[5] Three series of results are given, the first series (C.C.) are for a continuous current; the second (I.C.) are for a nearly perfect unidirectional intermittent current, obtained by employing a rectifier and bulb, and corresponding to a commutator making 3600 revolutions a minute; and the third (N) are those obtained by Newbery.[6] The first column gives the current density in milliamperes per sq. cm.

TABLE XXXIV

HYDROGEN OVERVOLTAGES FROM *N*-SULPHURIC ACID

Amperes 10^{-3} / Cm.^{2}	C.C.	I.C.	N.
	Lead		
150	1.23	1.05	0.56
50	1.18	1.01	0.64
10	1.11	0.98	0.71
	Nickel		
150	0.49	0.39	0.19
50	0.39	0.33	0.18
10	0.33	0.28	0.18

Newbery contends that the true counter electromotive force is only measured by the commutator method, and that when a continuous current is employed a film of hydrogen

[1] *Z. physik. Chem.*, **30**, 89 (1899).

[2] *Ibid.*, **50**, 641 (1905).

[3] *Ibid.*, **65**, 226 (1909).

[4] Newbery, *J. Chem. Soc.*, **105**, 2419 (1914); **109**, 1051 (1916); **109**, 1066 (1916); **109**, 1107 (1916); **109**, 1359 (1916); **111**, 470 (1917); **119**, 477 (1921); **121**, 7 (1922); Mem. Proc. Manchester Lit. Phil. Soc., 61, Parts II and III, Mem. No. 9 (1917).

[5] Glasstone, *J. Chem. Soc.*, **123**, 1745 (1923).

[6] *J. Chem. Soc.*, **109**, 1051 (1916); **109**, 1066 (1916).

is formed at the electrode which cannot diffuse away, and which causes an electric resistance, called "transfer resistance," to the flow of the current. This transfer resistance is thought to be the cause for the difference between the electromotive forces measured by the two methods. The transfer resistance varies greatly with change in current density, and is of physical origin. The electromotive force measured by the commutator method is the true chemical overvoltage, and varies little as a rule with change in current density. This point of view has also been adopted by Sand, Weeks, and Worrell.[1]

The existence of any appreciable transfer resistance at low current densities has been questioned by MacInnes,[2] Dunhill,[3] and others,[4] who attribute the observed difference to a potential which rapidly decreases when the current is interrupted. Glasstone ascribes the difference in electromotive forces measured by the two methods partially to an alternating induced current set up by the make and break of the intermittent current. It is well known that an alternating current superimposed on a direct current lowers the overvoltage at gas electrodes.[5]

Although considerable confusion arises from these experimental difficulties, it is possible, by measuring overvoltages by one experimental method, to arrive at some important but approximate conclusions regarding the relative overvoltages at cathodes of different elements (principally metals). If the commutator method be employed, Newbery found that, in the majority of cases, the overvoltage varied remarkably little for a change in current density from 2 to 2,000 milliamperes per sq. cm. cathode surface, while the direct current method gave very large variations. In Table XXXV are given a few characteristic measurements of hydrogen overvoltage at different current densities taken from Newbery's compilation.[6]

TABLE XXXV

CHARACTERISTIC OVERVOLTAGE DATA AT DIFFERENT CURRENT DENSITIES

Current Density	N-H_2SO_4				N-NaOH		
	Zn	Ni	Ir (*a*)	Ir (*b*)	Ni	Zn	Ir
2	0.68	0.16	0.01	0.18	0.18	0.59	0.43
10	0.69	0.18	0.03	0.18	0.20	0.60	0.44
50	0.71	0.18	0.04	0.18	0.21	0.59	0.44
100	0.71	0.19	0.05	0.18	0.21	0.59	0.45
1000	0.72	0.17	0.05	0.14	0.21	0.56	0.64
2000	0.72	0.15	0.08	0.12	—	—	0.63

[1] *J. Chem. Soc.*, **123**, 456 (1923).

[2] *J. Am. Chem. Soc.*, **42**, 2233 (1920).

[3] *J. Chem. Soc.*, **119**, 1081 (1921).

[4] Tartar and Keyes, *J. Am. Chem. Soc.*, **44**, 557 (1922).

[5] Grube and Dulk, *Z. Elektrochem.*, **24**, 237 (1918); Goodwin and Knoble, *Trans. Am. Electrochem. Soc.*, **37**, 617 (1920).

[6] *J. Chem. Soc.*, **109**, 1051 (1916); **109**, 1107 (1916).

The values of the overvoltage of hydrogen on both zinc and nickel are roughly the same in both the sulphuric acid and sodium hydroxide solutions. This was found to be the case with the many other electrodes examined. The results with iridium cathodes are particularly interesting. The four distinct values, 0.18, 0.06, 0.45, and 0.67, were found by Newbery. The same phenomenon was observed in the case of electrodes of other elements which possess more than one valence. The direct current method does not give these discontinuities. Table XXXVI contains the hydrogen overvoltages for all the elements measured by Newbery, arranged according to the groups of the periodic system.

TABLE XXXVI

HYDROGEN OVERVOLTAGES OF ELEMENTS

Group	Element	Overvoltages			
I	Cu	0.34			
	Ag	0.30			
	Au	0.36	(0.12)		
II	Mg	0.70			
	Zn	0.72			
	Cd	0.66	(0.50)		
	Hg	0.70	(0.53)		
III	Al	0.50	(0.19)		
	Tl	0.52			
IV	C (graphite)	0.35	(0.64)		
	Sn	0.45	(0.66)		
	Pb	0.42	(0.69)		
V	Sb	0.43	(0.67)		
	Ta	0.42			
	Bi	0.42	(0.76)		
VI	Cr	0.38			
	Mo	0.32			
	W	0.30			
VII	Mn	0.33	(0.57)		
VIII	Fe	0.27	(0.35)		
	Ni	0.24			
	Co	0.26	(0.69)		
	Rh	0.02	(0.08)		
	Pd	0.07	(0.58)		
	Ir	0.18	(0.04)	(0.45)	(0.67)
	Pt	0.18	(0.06)	(0.45)	(0.65)

The values which are not in brackets are taken by Newbery to be the principal overvoltage of the group, while the others are secondary. Each group of the periodic system has its definite overvoltage, a result which is hardly fortuitous, and which, as pointed out by Newbery, seems to link the overvoltage of hydrogen with the valence of the element employed as cathode.

Theories of Hydrogen Overvoltage: Many theories have been proposed to account for hydrogen overvoltage. These theories may be divided into three classes, which in turn attribute the cause of hydrogen overvoltage to purely physical factors, to chemical changes on electrodes, and to the velocity of electrode processes.

Let us first consider the purely physical factors which have been regarded either partially or completely to determine the overvoltage. Haber [1] proposed that the phenomenon is caused by a poorly conducting hydrogen layer of varying thickness. In more recent studies, such a layer is thought by some investigators to produce a "transfer resistance" but not to account for all the overvoltage. Müller [2] found that overvoltage depends on bubble formation. That this is the case, to some extent at least, during continuous current electrolysis has been interestingly shown by MacInnes and Adler [3] who determined the overvoltage of hydrogen on platinized platinum at very low current densities. They noticed a distinct periodicity of the overvoltage, which rose and fell between the limits of 1.6 and 1.9 millivolts, as the electrolysis proceeded. Every time that the overvoltage reached 1.9 millivolts, a bubble had separated at one point on the electrode leaving a small nucleus. As this nucleus grew in size, the voltage dropped, and then rose rapidly when the bubble again separated. Each rise and fall was associated with the formation and evolution of a single bubble. It is a matter of considerable importance that the formation of a minute bubble can determine the potential of an electrode many thousand times the area of the bubble.

On equating the molal electrical energy, obtained from the electromotive force measurement, with the energy necessary to form one mol of hydrogen bubbles of radius r, MacInnes and Adler obtained the equation

$$\mathbf{E} = \frac{6RT}{pr\mathbf{F}}\gamma,$$

where $\mathbf{E}$ is the overvoltage, p the pressure, γ the surface tension, the other symbols having their usual significance. They determined the bubble radius by a microscopic method, and found that the values of $\mathbf{E}$, calculated by the above equation, agreed approximately with the observed results. The effect of pressure on the overvoltage could also be predicted by means of this equation.

As a result of this investigation, MacInnes and Adler [4] have proposed the theory that hydrogen overvoltage is caused by a layer of supersaturated solution of dissolved hydrogen in the immediate neighborhood of the electrode. If an electrode adsorbs hydrogen, this layer cannot reach a high degree of supersaturation and the overvoltage will be low. Metals which do not adsorb hydrogen readily will have a high overvoltage.

Other factors of a physical nature have been found which may influence the hydrogen overvoltage to an unknown extent. For instance, Newbery found that electrodes after prolonged use as cathodes exhibited rough surfaces on microscopic examination. Tiny craters were formed on the surface, a fact which indicated that the hydrogen entered the metal, developed a high pressure, and produced surface disintegration. Any increase in pressure of the

[1] *Z. Elektrochem.*, **8**, 539 (1902).
[2] *Z. physik. Chem.*, **65**, 226 (1909).
[3] *J. Am. Chem. Soc.*, **41**, 194 (1919).
[4] Also MacInnes and Contieri, *J. Am. Chem. Soc.*, **41**, 2013 (1919).

hydrogen in or on the electrode would increase the overvoltage. Further, the gas which escapes during electrolysis is ionized. Newbery suggested that the ionized gas probably produces an electromotive force by induction. His investigation of this effect indicated that this electromotive force was opposite in sign to the overvoltage.

There is only one chemical theory of hydrogen overvoltage. Newbery contends that hydrogen overvoltage, (the true counter electromotive force, after the effects caused by transfer resistance, etc., have been eliminated), is primarily caused by the formation of unstable hydrides of high electrical conductivity on the electrode surfaces. The overvoltage corresponds to the free energy of formation of these hydrides. The nature of the hydride depends on the valence of the element employed as cathode. Multivalent elements have more than one hydride, and, consequently, have more than one overvoltage. This explains the dependence of overvoltage on valence, which is illustrated in Table XXXVI. As further evidence of this theory, Newbery points out that stibine may be formed at an antimony cathode by electrolysis of both sulphuric acid and sodium hydroxide solutions. Under similar conditions, hydrocarbons form at a carbon cathode. The formation of stibine under these conditions has been recently investigated comprehensively by Sand, Weeks, and Worrell.[1] Some evidence was likewise obtained by Newbery for the existence of hydrides at some metallic electrodes such as magnesium, cadmium, and copper. In connection with this theory, it is possible that the electrolysis might produce an adsorbed layer of hydrogen atoms, orientated on the electrode surface. In other words, the "hydrides" would not necessarily have to be in a truly molecular condition.

Many theories have been proposed which assign the cause of overvoltage to the retardation of electrode processes. If we suppose that the reaction

$$H^+ + \Theta \rightarrow \tfrac{1}{2}H_2$$

represents the electrode process, it is clear that any factor which would retard this reaction would increase the overvoltage. Nernst [2] suggested that such a retardation would be effected by the slowness with which an electrode which had adsorbed the gas could come in equilibrium with the surroundings.

According to Bancroft [3] and Bennett and Thomson,[4] monatomic hydrogen is formed during the process, which combines to form molecular hydrogen according to the mechanisms

$$(1)\quad H^+ + \Theta \rightarrow H \qquad \text{and} \qquad (2)\quad 2H \rightarrow H_2.$$

If reaction (2) is slow, hydrogen atoms will accumulate and give rise to a greater counter electromotive force. It is possible that the metal electrodes might have specific catalytic effects on these reactions, thus producing different over-

[1] *J. Chem. Soc.*, **123**, 456 (1923).
[2] *Ber.*, **30**, 1547 (1897).
[3] *J. Phys. Chem.*, **20**, 396 (1916).
[4] *Ibid.*, **20**, 296 (1916); *Trans. Am. Electrochem. Soc.*, **29**, 24 (1916).

voltages. Rideal [1] has suggested another theory of these processes. Monatomic hydrogen is first formed but immediately reacts to form molecular hydrogen. Overvoltage is a measure of the free energy or work necessary to remove the molecular hydrogen from the metal surfaces.

Smits' Theory of Polarization Phenomena: The application of Smits' theory of electromotive equilibria to polarization phenomena differs to a considerable extent from any of the theories just discussed. Indeed, Smits explains cathode polarization and anode polarization of metals and gases in general by postulating a disturbance of the inner equilibrium of the metal or gas phase.

Let us first consider what may occur at the cathode and anode when, for example, a solution of copper sulphate is electrolyzed between electrodes of copper. To simplify matters, let it be assumed that the copper ion concentration remains the same throughout the solution. Before electrolysis takes place, the heterogeneous equilibrium at each electrode surface will be

$$\begin{array}{ccccc} Me_s & \rightleftharpoons & Me_s^{\nu+} + \nu\Theta_s, \\ \Updownarrow & & \Updownarrow \quad \Updownarrow \\ Me_l & \rightleftharpoons & Me_l^{\nu+} + \nu\Theta_l. \end{array}$$

Smits assumes that the heterogeneous equilibria, $Me_s \rightleftharpoons Me_l$, $Me_s^{\nu+} \rightleftharpoons Me_l^{\nu+}$, and $\nu\Theta_s \rightleftharpoons \nu\Theta_l$, will always be established instantaneously. During electrolysis, electrons will be supplied to the cathode from the external circuit, and metallic ions will be deposited. Metal atoms will form according to the scheme:

$$\begin{array}{ccc} & & \nu\Theta \\ & & \downarrow \\ Me_s^{\nu+} & + \nu\Theta_s \rightarrow & Me_s. \\ \uparrow & & \\ Me_l^{\nu+} & & \end{array}$$

If the homogeneous reaction

$$Me_s^{\nu+} + \nu\Theta_s \rightarrow Me_s$$

takes place so rapidly that $\nu\Theta_s$ disappears to form Me_s as rapidly as $\nu\Theta$ enters the cathode, the inner equilibrium concentrations will be maintained, and the potential of the electrode will not change. But, if this latter reaction takes place slowly, then the metal surface will contain an excess of electrons and ions, and $Me_s^{\nu+}$ will be greater than $Me_l^{\nu+}$. The electrode will then possess a greater tendency to give off ions and its potential will be more positive. We have already found that metals such as iron, cobalt, and nickel, when deposited electrolytically, have a higher potential than in the normal state. Indeed, the overvoltage of these metals was found to be a function of their physical state, which would in turn depend on the extent to which the inner state of the system is displaced from the stable equilibrium state. According to the theory of Smits, the above homogeneous solid reaction would be slow in the cases of iron, cobalt, and nickel, and rapid for copper, lead, etc.

[1] *J. Am. Chem. Soc.*, **42**, 94 (1920).

Just the opposite occurs at the anode where electrons are drawn into the external circuit. The anode process will be

$$\begin{array}{c} \nu\Theta \\ \uparrow \\ Me_s^{\nu+} + \nu\Theta_s \leftarrow Me_s. \\ \downarrow \\ Me_l^{\nu+} \end{array}$$

If Me_s will supply electrons as rapidly as they are removed, polarization will not occur. If the reaction

$$Me_s \rightarrow Me_s^{\nu+} + \nu\Theta$$

is slow, the anode surface will contain less electrons and ions than correspond to inner equilibrium, and the metal to solution electrode potential will become more negative. These homogeneous reactions may be influenced by catalysts. The presence of oxygen gas, according to Smits, retards, the presence of hydrogen gas or the chloride ion accelerates this last reaction.

The electrolytic overvoltage of hydrogen is due to the same cause as metal cathode overvoltage. In depositing hydrogen, the homogeneous reaction in the gas phase

$$2H_g^+ + 2\Theta_g \rightarrow H_{2g}$$

takes place. If this reaction does not occur as rapidly as electrons are supplied, the gas will contain more ions and electrons than under inner equilibrium conditions. As with metal deposition, since H_g^+ will be greater than H_l^+, the hydrogen electrode potential corresponding to such a disturbance will be more positive.

Anodic Overvoltage during Gas Deposition: The phenomenon of overvoltage which was found to occur during the deposition of hydrogen and metals likewise occurs during the deposition of other gases. The overvoltage of chlorine from normal hydrochloric acid will equal the electromotive force of the cell

$$Mc\ (Cl_2\ \text{depositing}) \,|\, HCl\ (N) \,|\, Cl_2 \,|\, Pt; \qquad \mathbf{E} = \text{negative value},$$

where $Cl_2 \,|\, Pt$ is the reversible chlorine electrode. Chlorine overvoltages have recently been investigated by Newbery.[1] Carbon, rhodium, iridium and platinum are unattacked by the chlorine. Gold and palladium are attacked readily at low current densities. When higher current densities are employed (200 milliamperes per sq. cm. for gold and 50–100 milliamperes per sq. cm. for palladium), reaction of chlorine on the metal stops, chlorine gas is evolved freely, and the potential changes more than 0.5 volt. Under these conditions, the metals are in the "passive state" and are not attacked by the chlorine.

For the metals in the passive state or for the non-corrodible electrodes, Newbery found that the overvoltage of chlorine had the same value as the

[1] *J. Chem. Soc.*, 119, 477 (1921).

overvoltage of hydrogen. He concludes that chlorine overvoltage as well as hydrogen overvoltage is a function of the valence of the element. Platinum shows three distinct overvoltages which are 0.0, 0.18, and 0.45 volt. Intermittent current electrolysis was employed throughout this investigation.

The overvoltage of oxygen is equal to the electromotive force of the cell

$$\text{Me}(O_2 \text{ depositing}) \,|\, \text{NaOH or } H_2SO_4 \text{ etc.} \,|\, O_2 \,|\, \text{Pt}; \qquad \mathbf{E} = \text{negative value},$$

where $O_2 \,|\, \text{Pt}$ is the reversible oxygen electrode. In Table XXXVII are given some of the values of oxygen overvoltages obtained by Newbery by the intermittent current method. The direct current method yields somewhat higher results.[1] Normal solutions of sodium hydroxide and sulphuric acid were employed.

TABLE XXXVII

OXYGEN OVERVOLTAGES

Metal	Overvoltage = (− E)	Metal	Overvoltage = (− E)
Cu	0.62	Co	0.55
Ag	0.71	Pd	0.65
Zn	0.93	Ir	0.48
Pb	0.94	Pt	0.86
Ni	0.57	Mn	0.92

These anode overvoltages compared to the oxygen electrode are invariably higher than the hydrogen overvoltages in the case of a given metal electrode.

Passivity of Metals and Anodic Polarization: The fact that after iron is dipped into strong nitric acid it resists the action of dilute acids has been known for a long time.[2] The nitric acid changes the surface of the iron and renders it "passive." Ordinary or active iron possesses an electrode potential 0.390 volt more positive than copper and 0.845 volt more positive than silver, and, therefore, will replace both these metals from solutions of their salts. When iron becomes passive, its potential becomes more negative, or is changed in the direction of the potential of the noble metals. In the passive state, iron will not precipitate copper or silver from solutions of their salts. The same is true of cobalt, nickel, and chromium. If passive iron is washed with pure water, alcohol, and ether, and dried in the presence of air, it remains passive. In a vacuum, it becomes active. Passive iron has never been obtained in the absence of air.

Metals may be caused to lose their passivity in many ways. This may be most strikingly demonstrated by rendering passive, by dipping into strong nitric acid, a clean and well-polished sheet of iron, held by a glass hook. The surface is then covered with a copper sulphate solution by immersing in a solution of that salt. No copper will be precipitated. If any part of the metal be scratched with a piece of glass, copper will be precipitated at the scratch and the precipitation will proceed from the scratch over the entire surface very rapidly. A blow will bring about the same result. Contact with active iron, or any metal such as nickel, cobalt, or magnesium, which has a higher electrode potential, will produce

[1] Glasstone, *J. Chem. Soc.*, **123**, 1745 (1923).

[2] Keir, *Phil. Trans.*, **80**, 374 (1790).

the same result. Noble metals such as gold or platinum will not cause activation. As a matter of fact, their presence in contact with the iron is thought to help to induce passivity. The same type of phenomena occurs when a silver nitrate solution is employed instead of a copper sulphate solution. In this case, the activation spreads more slowly over the surface, and may be clearly seen to proceed from the areas disturbed by the contact. Nickel and cobalt behave in a similar manner.

Passive metals may be rendered active by contact with solutions containing halogen ions. Thus, if the tip of the passive iron sheet, covered with the copper sulphate solution, be immersed in a solution containing the chloride, bromide, or iodide ion, activation will proceed from the immersed part over the entire surface. Usually, in this case, there will be a short induction period, which is probably due to the time required for the halogen ions to diffuse through the copper sulphate solution. Passive metals are also rendered active by increase in temperature.

When certain metals are made the anode in acid or basic solutions, passivity is brought about by electrolysis, and when the change from the active to the passive form takes place, it is accompanied by a large increase in counter electromotive force. In some cases, it seems obvious that passivation is due to the formation of an oxide. Thus, lead passivates readily in acid solutions at low current densities, and at the same time becomes coated with a layer of the dioxide. At low current densities a silver anode remains active. A current density of 50 milliamperes per sq. cm. causes passivity and the counter electromotive force changes by more than a volt in a few seconds. If the current density be lowered to 20 milliamperes per sq. cm., the anode slowly regains its activity. At a current density of 40 milliamperes per sq. cm., a periodic rise and fall of the counter electromotive force is observable. In thirty seconds the rise is about 0.6 volt, and a corresponding fall takes place in about two and one half minutes.[1] In sulphuric acid solution nickel becomes passive at a current density of about 100 milliamperes per sq. cm. At 50 milliamperes there is a periodic change in the potential of the electrode. The potential changes about 1.1 volts and the period of fall or rise is about six seconds. When iron, cobalt, or nickel are rendered passive by electrolysis or by concentrated nitric acid, there is no visible change of appearance of the metallic surface.

Another interesting example of periodic passivation has been carefully investigated by Smits and de Bruyn [2] who used a photographic method to record the phenomenon. The electrolyte consisted of a solution containing ferrous, sulphate, and chloride ions. The chloride ions will render passive iron active, and the electrolysis will cause passivation. The net result is a periodic passivation and activation with a corresponding periodic change in anode potential of 1.74 volts. The duration of successive periods of fluctuation is about 6 seconds.

Theories of Passivity: Many investigators [3] have supported the view that passivity is caused by the presence of an oxide film on the surface of the metal

[1] Newbery, *J. Chem. Soc.*, **109**, 1066 (1916).

[2] Versl. Kon. Akad. v. Wet. Amsterdam, **24**, 745 (1915); **27**, 159 (1918).

[3] Faraday, *Phil. Mag.*, (3) **9**, 122 (1836); Haber and Goldschmidt, *Z. Elektrochem.*, **12**, 49 (1906); Bennett and Burnham, *Trans. Am. Electrochem. Soc.*, **29**, 38 (1916); Newbery, *J. Chem. Soc.*, **109**, 1107 (1916); **109**, 1359 (1916).

CHAPTER XIII

ELECTROMETRIC METHODS IN ANALYTICAL CHEMISTRY

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One of the most prominent developments of the analytical chemistry of the present century has been the study and perfection of numerous and varied applications of physico-chemical measurement to the solution of analytical problems. The foundation of the majority of these methods is the electrolytic dissociation theory of Arrhenius, together with the subsequent brilliant developments in the field of electro-chemistry.

Consequently, methods of electrical measurement, with their attendant ease, rapidity, and precision, have been shown to be especially adapted to the study of analytical, as well as other processes which occur in aqueous solution. We shall turn our attention first to perhaps the most important single factor in nearly all of these processes, namely degree of acidity as represented by hydrogen-ion concentration measurements.

THE MEASUREMENT OF HYDROGEN-ION CONCENTRATION

General Relations of Acids and Bases: If we represent the electrolytic dissociation of an acid by the equation:

$$HA \rightleftharpoons H^+ + A^-, \tag{1}$$

the equilibrium relations in sufficiently dilute aqueous solution at constant temperature are expressed by the Mass Action relation:[1, 2]

$$\frac{[H^+][A^-]}{[HA]} = K_a, \tag{2}$$

where $[H^+]$, $[A^-]$, and $[HA]$ represent molecular concentrations of hydrogen ion, anion, and undissociated molecule respectively.

In general the value of the dissociation constant, K_a, does not vary much with moderate changes in temperature. The order of magnitude of the constant is a characteristic and important property of each acid. Weak and extremely weak acids (K_a varies from 2×10^{-5} for the former to about 10^{-10} for the latter) give well-defined constants over a large range of dilution. The

[1] See Chapter VIII for the theoretical development of the Law of Mass Action.

[2] Ostwald, *Z. physik. Chem.*, 2, 278 (1888), was the first to apply the Mass Law considerations to the phenomena of electrolytic dissociation.

moderately weak and moderately strong acids give fairly well-defined constants over limited dilution ranges. The highly dissociated acids (HCl, HNO_3, HBr, HI, H_2SO_4, etc.) do not yield constant values even over limited ranges in quite dilute solution. This is due to the disturbing influence of various factors —hydration of ions, electrostatic effects, etc.– whose exact effect is not yet fully understood.[1]

Polybasic Acids: Acids which contain more than one replaceable hydrogen atom per molecule exhibit two, three, or more dissociation steps, each of which possesses a characteristic dissociation constant, K_a. Each step corresponds to the ionizing tendency of one of the variously bound hydrogen atoms. In the case of oxalic acid, for example, the equilibria are:

$$\frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]} = K_1 \qquad (K_1 = 1.0 \times 10^{-1}) \tag{3}$$

and

$$\frac{[H^+][C_2O_4^{=}]}{[HC_2O_4^-]} = K_2 \qquad (K_2 = 4.1 \times 10^{-5}). \tag{4}$$

Combining (3) and (4) we have:

$$\frac{[H^+]^2[C_2O_4^{=}]}{[H_2C_2O_4]} = K_1 \times K_2 = K.$$

In general as in this instance the value of the first constant is greater than that of the second. For tribasic acids the relative order of magnitude of the constants is $K_1 > K_2 > K_3$, etc.

Bases: Entirely analogous relations hold true in the case of basic substances. If we represent the electrolytic dissociation of a base by the equation:

$$BOH \rightleftharpoons B^+ + OH^-, \tag{5}$$

the equilibrium expression is

$$\frac{[B^+][OH^-]}{[BOH]} = K_b. \tag{6}$$

Highly dissociated bases do not yield a constant K_b value.

Dissociation of Water:[2] The dissociation of water into hydrogen and hydroxyl ions, although extremely slight in magnitude, is a factor of great importance in many of the reactions which occur in aqueous solution. The mass law relation:

$$\frac{[H^+][OH^-]}{[H_2O]} = K \tag{7}$$

[1] See Anomaly of Strong Electrolytes, Chapter XI.

[2] For various methods of measuring this dissociation see Chapter XI. The dissociation of hydroxyl ion into oxygen and hydrogen ion is of interest in considering the nature of oxidation potential.

may be replaced by the simpler expression:

$$[H^+][OH^-] = K_w \tag{8}$$

because the concentration of molecular water may be regarded as unchanged by this extremely slight ionization.

At temperatures from 20 to 25° C. $K_w = 1.0 \times 10^{-14}$ (approx.). It is a fact of extreme importance for hydrolytic reactions that the value of K_w increases some sixty-fold when the temperature is increased from 20° to the boiling point. In water, or in any neutral aqueous solution at room temperature:

$$[H^+] = [OH^-] = 10^{-7}.$$

We may therefore speak of the hydrogen- or hydroxyl-ion concentration of any solution however acidic or basic it may be, since the product of these concentrations is always equal to K_w.

The Hydrogen-Ion Exponent Scale: In order to single out and emphasize the importance of hydrogen-ion concentration, Sörensen [1] suggested that the numerical values of the negative exponents of hydrogen-ion concentration values be adopted as the basis of a $[H^+]$ scale. He recommended the symbol P_H. We shall employ the simpler symbol, pH, which Clark proposed.[2] The general relation is therefore:

$$\text{pH} = \log \frac{1}{[H^+]} \qquad \text{or} \qquad [H^+] = 10^{-\text{pH}}. \tag{9, 9a}$$

In a solution which is 0.0001 N with respect to hydroxyl ion, we have:

$$[H^+] = \frac{10^{-14}}{10^{-4}} = 10^{-10}.$$

Hence pH = 10. Table I will serve to illustrate the relationship further.

TABLE I

THE RELATIONSHIP BETWEEN pH AND $[H^+]$ VALUES.

Hydroxyl-ion conc.	10^{-13}	10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}
Hydrogen-ion conc.	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}
pH	1	3	5	7	9	11	13

All hydrogen-ion concentration values may thus be expressed upon an exceedingly simple continuous scale. It is sometimes convenient to refer to the pOH values of solutions. pH + pOH = 14.

The Hydrolysis of Salts. The degree of hydrolytic action in a salt solution depends upon the nature of the salt and upon the temperature. If we represent the general reaction by:

[1] *Biochem. Z.*, **21**, 131 (1909).

[2] Clark, "The Determination of Hydrogen Ions," 2d Edition, p. 35 (1922). Williams and Wilkins Co., Baltimore, Md. A comprehensive monograph of 480 pp. containing an extensive bibliography.

(10) $$BA + H_2O \rightleftharpoons BOH + HA,$$

then the equilibrium expression is:

(11) $$\frac{[HA][BOH]}{[BA]} = K_{hyd.}$$

The molecular concentration of water is regarded as constant. By substituting the respective equilibrium values for [HA], [BOH], and [BA], we have:

(12) $$\frac{[HA][BOH]}{[BA]} = \frac{K_{BA}K_w}{K_aK_b} = K_{hyd.}$$

This general expression is of little utility because of the difficulty of determining the various concentrations, and because strong electrolytes do not yield mass law constants. Special equations may be derived from (12) by making assumptions to fit individual instances. We shall consider the most important special cases.

(*a*) Salts of strong acids and bases are not hydrolyzed to any appreciable degree. The hydrogen-ion concentration of such solutions lies close to 10^{-7} in general, and will equal this value in the event that $K_a = K_b$.

(*b*) If one constituent of the salt is derived from a weak, and the other from a strong, acid or base, we have a case which is of general interest and of especial importance from the standpoint of neutralizations, precipitations, etc. Representing the reaction for the salt of a strong base and weak acid by:

(13) $$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA,$$

the equilibria which must be simultaneously satisfied are:

$$\frac{[H^+][A^-]}{[HA]} = K_a \qquad \text{and} \qquad [H^+][OH^-] = K_w.$$

If we define the degree of hydrolysis (γ) as the fraction (of the total salt taken) which has undergone hydrolysis, it is evident that:

(14) $$[HA] = \gamma C$$

(C being the total amount of salt per unit volume, i.e., liter),

(14a) $$[OH^-] = \alpha_b\gamma C$$

(α_b being the degree of dissociation of the base),

(14b) $$[A^-] = \alpha_{ba}(1 - \gamma)C.$$

The combination of these five relations yields the formula:

(15) $$\frac{\alpha_bC\gamma^2}{\alpha_{ba}(1 - \gamma)} = \frac{K_w}{K_a}.$$

In making approximate calculations we may assume that $\alpha_b = \alpha_{ba}$, and that $(1 - \gamma)$ is not sensibly different from 1. The equation then becomes:

$$\gamma = \sqrt{\frac{K_w}{K_a C}}. \tag{16}$$

If the salt were one of a strong acid and weak base, equation (16) would apply upon substituting K_b for K_a.

Bjerrum [1] has derived equation (16) in a slightly different manner, to calculate moderate degrees of hydrolysis (less than one per cent), the hydroxyl-ion concentration being $> 10^{-6}$. Bjerrum (l.c.) also derived the following expressions (17 and 18) for very weak, or for very marked, degrees of hydrolysis respectively:

Assuming that for salts of the weak acid-strong base type $\gamma = \frac{[OH^-]}{C}$, and for the reverse type of salt $\gamma = \frac{[H^+]}{C}$, he finds for instances of very slight hydrolysis (less than one per cent), the hydroxyl-ion concentration being less than 10^{-6}:

$$\gamma = \sqrt{\frac{K_w}{K_a C}\left(1 + \frac{K_a}{C}\right)}. \tag{17}$$

(Or for a salt of the strong acid-weak base type, substitute K_b for K_a, and read hydrogen-ion concentration less than 10^{-6}.)

In instances of very considerable hydrolysis, i.e., greater than one per cent, the hydroxyl-ion concentration being greater than 10^{-6}, he derives the equation:

$$\gamma = \frac{\sqrt{\frac{K_w}{K_a C}}}{\sqrt{1 + \frac{K_w}{4K_a C}} + \sqrt{\frac{K_w}{4K_a C}}}. \tag{18}$$

(For a salt of a strong acid-weak base, substitute K_b for K_a, and read hydrogen-ion concentration being greater than 10^{-6}.)

With the aid of equations (16–18) Bjerrum calculated the degree of hydrolysis as affected by the dissociation constant (of the weaker constituent of the salt) and the degree of dilution at room temperature ($K_w = 10^{-14}$). These values have been transferred to the pH scale by Michaelis.[2]

[1] Bjerrum, *Ahrens Sammlung*, **21**, 12 (1915). A monograph of 128 pages entitled "Die Theorie der alkalimetrischen und azidimetrischen Titrierungen."

[2] Michaelis, "Die Wasserstoffionen Konzentration," I, p. 77. 2d Edition (1922). Julius Springer, Berlin. (A 262 page monograph.)

TABLE II

DEGREE OF HYDROLYSIS AT VARIOUS CONCENTRATIONS

The numbers are pH values for the salts of weak base-strong acid type, or pOH values for the salts of weak acid-strong base type

Dissoc. Const. of the weaker constituent	Normality of Solution			
	1.0	0.1	0.01	0.001
∞	7	7	7	7
10^{-2}	6	6.5	6.9	7
10^{-4}	5	5.5	6.0	7
10^{-6}	4	4.5	5.0	6
10^{-8}	3	3.5	4.0	4.5
10^{-10}	2	2.5	3.0	3.6
10^{-12}	1.02	1.6	2.2	3.0

(These values as well as those of Bjerrum are rounded values.) By interpolation any desired dissociation constant may be considered. For example, let us calculate the degree of hydrolysis of 0.1 N sodium acetate solution. $K_a = 1.8 \times 10^{-5}$. By graphic interpolation, plotting $-\log K$ against pOH, we find pOH to be 5.1 (approx.). Hence,

$$\gamma = \frac{10^{-5.1}}{10^{-1}} = 10^{-4.1} = 0.74 \times 10^{-5}.$$

Shields[1] found experimentally 0.008 per cent (or 0.8×10^{-5}).

(*c*) Salts, which are derived from acids and bases which are both weak, undergo a rather extensive hydrolysis; the reaction of the solution remains close to neutral, however, since the dissociation constants are often nearly equal, and the degree of dissociation slight. The general hydrolysis equation (12) reduces in this instance to the form:

$$\frac{[\mathrm{BOH}][\mathrm{HA}]}{K_{ba}[\mathrm{BA}]} = \frac{K_w}{K_a K_b}. \tag{19}$$

Obviously,

$$K_{ba}[\mathrm{BA}] = [\mathrm{B}^+][\mathrm{A}^-],$$

and, if we make the assumption that the salt is completely dissociated, (19) becomes:

$$\gamma = \sqrt{\frac{K_w}{K_a K_b}}. \tag{20}$$

As a first approximation, salts of this type give a constant degree of hydrolysis regardless of the degree of dilution.

[1] *Z. physik. Chem.*, **12**, 167 (1893).

The Hydrogen Electrode

The most precise experimental method for the study of the relation of hydrogen-ion concentration to various chemical processes consists in the measure of the electromotive force of a cell composed of a hydrogen electrode and a suitable reference electrode, both of which are in electrolytic contact with the solution under examination.[1] This method of attack yields important information regarding various analytical problems, for example, the determination of exact conditions of precipitation, the general course of neutralizations, the choice of indicators, the study and control of electrodeposition processes.

The reference electrode is usually either the 0.1 normal, the normal, or the saturated calomel electrode. The normal, or 0.1 normal hydrogen electrode may also be used as a reference standard. The observed difference of potential for a cell composed of a reference electrode and a hydrogen electrode may be regarded as the sum of two differences of potential, viz., (1) between the reference electrode and a normal hydrogen electrode, and (2) between the normal hydrogen electrode and the hydrogen electrode which is immersed in the unknown solution.

$$\text{Observed E.M.F.} \left\{ \begin{array}{ll} \left.\begin{array}{l} \\ \\ \end{array}\right\} E_{\text{ref.}} & \text{(Usually calomel electrode.)} \\ \left.\begin{array}{l} \\ \\ \end{array}\right\} D_1 & \\ \left.\begin{array}{l} \\ \\ \end{array}\right\} {}_oE_h & \text{(N hydrogen electrode.)} \\ \left.\begin{array}{l} \\ \\ \end{array}\right\} D_2 & \\ \left.\begin{array}{l} \\ \\ \end{array}\right\} E_h & \text{(Electrode in sol'n. of unknown pH.)} \end{array} \right.$$

The first difference, D_1, is a constant for any given reference electrode at constant temperature. The second, D_2, is expressed by the familiar Nernst formula:

$$ {}_oE_h - E_h = \frac{RT}{nF} ln \underset{\text{Const.}}{1} - \frac{RT}{nF} ln \underset{\text{Const.}}{[H^+]} .$$

Upon substituting the values of R, n, and F in electrical units, and at the same time converting to common logarithms (Briggs' system), we have the following equation for relating observed electromotive force, hydrogen-ion concentration, and pH:

$$(21) \qquad \begin{aligned} E_{\text{Obs.}} &= \text{Constant} + 0.000198T \log \frac{1}{[H^+]} \\ &= \text{Constant} + 0.000198T \text{ pH}. \end{aligned}$$

At 25° C. the constant has the values 0.3359, 0.283, 0.245, or 0.0000, respectively, if an 0.1 normal, or saturated calomel, or N hydrogen electrode is used as the standard of reference.[2] Equation (21) does not take into account the

[1] The general theory of electrode potentials is discussed in Chapter XII.

[2] These values are derived from the results of Fales and Vosburgh, *J. Am. Chem. Soc.*, **40**, 1291 (1918), Fales and Mudge, *ibid.*, **42**, 2434 (1920). The fixing of the standard of reference involves the assumption of a degree of ionization of an acid solution. For a discussion of the present status of the standardization of hydrogen-ion measurements, see Clark, *loc. cit.*, p. 276 and ff.

liquid junction potential between the solution of the reference electrode and the solution under examination. The interposition of a concentrated "salt bridge" may minimize, or virtually eliminate, this difference of potential. The hydrogen must be supplied at atmospheric pressure.

The Nernst electrode potential formula applies only to ideally dilute solutions. By employing the Lewis activity concept [2] the correlation between observed and calculated values for the activity of the hydrogen ion may be extended to solutions as concentrated as three molar in many instances. The relations which are of significance from the analytical standpoint would not be altered by employing the activity concept; in what follows, therefore, we shall assume that equation (21), with corrections for liquid junction potential and variations of hydrogen pressure from one atmosphere, gives a valid interpretation of the electromotive force measurements.

The Course of Neutralizations: Methods for the precise measurement of electromotive forces have been discussed in Chapter X.

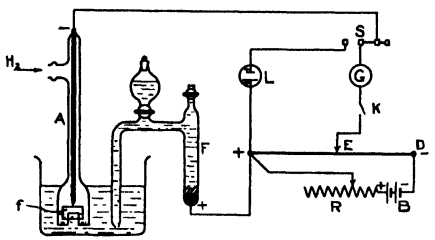


FIG. 1. Apparatus for Potentiometric Titration, or for Determination of Hydrogen-Ion Concentration.

For analytical purposes a simple potentiometer will ordinarily suffice, since liquid potential errors and slight temperature variations do not obscure the general relationships. Fig. 1 illustrates a convenient apparatus. The hydrogen electrode, *A*, is of the type devised by Hildebrand.[3] The platinized foil, *f*, is half immersed in the solution. The cell is completed by means of the side tube of the calomel cell (*F*) which dips into the beaker. *CD* is a slide wire of uniform cross-section. A suitable fall of potential is maintained from *C* to *D* by means of a battery *B* and the rheostat, *R*. Equal divisions of the length of the wire may be made to represent equal subdivisions of a volt, as hundredths, thousandths, etc., upon proper adjustment of *R*. By means of the switch, *S*, either the unknown E.M.F. or the standard cell may be connected with the potential divider, *CD*. The unknown E.M.F. is determined from the proportion: E.M.F. : Total voltage drop *C* to *D* as distance *CE* : *CD*.

We may measure the E.M.F. in this manner upon successive small additions of acid or alkali in a titration. Upon plotting the E.M.F. values as ordinates (or preferably the pH values derived by the use of equation (21)), and cubic centimeters of reagent as abscissæ, we obtain titration graphs (Figs. 2, 3, 4 and 6) which throw much light upon the general nature of acidity. Fig. 2 serves to contrast the behavior of a strong with that of a weak acid. The titration graph of any strong acid with a strong base consists of a relatively flat portion (*a*) until the equivalent point is approached, because the hydrogen-ion concentration does not change in order of magnitude rapidly in this region, owing to the high degree of dissociation of the acid. As the last traces of

[1] See Chapter XII for methods of calculating liquid potential values.

[2] Lewis, *J. Am. Chem. Soc.*, **34**, 1631 (1912) and other papers. See Chapter XII.

[3] Hildebrand, *J. Am. Chem. Soc.*, **35**, 849 (1913).

hydrogen ion are neutralized, its concentration passes very rapidly through ten-fold changes in value, and the curve exhibits an almost vertical rise (*b*) whose mid-point is very closely pH = 7. As excess of alkali is added, a second relatively flat portion (*c*) follows. Weak acids, on the other hand, undergo rapid changes in hydrogen-ion concentration upon successive small additions of alkali at the start, because of the initial slight dissociation of the acid. The salt which is formed exerts a significant mass action and causes a flattening out of the curve. At the equivalent point, there is a nearly vertical rise, which is shorter in this instance. The position of the mid-point of the rise depends

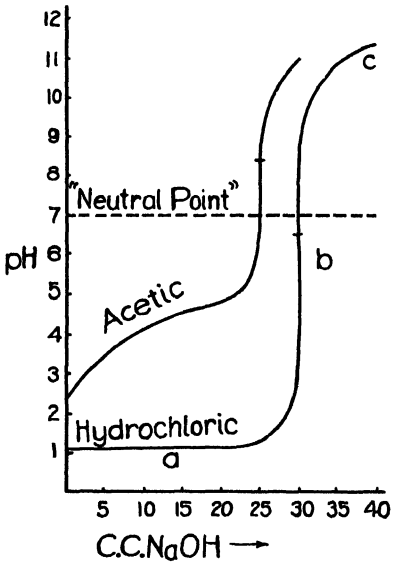


FIG. 2. Titration of 25 cc. of acetic acid and of 30 cc. of hydrochloric acid with alkali of equivalent strength. Note. The curves in this and subsequent figures are plotted from the author's data, unless otherwise noted.

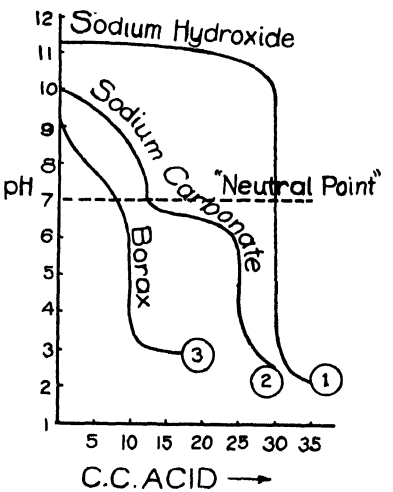


FIG. 3. Titration of 30 cc. NaOH solution (1), 25 cc. Na_2CO_3 solution (2), and 10 cc. borax solution (3), with acid solutions of equivalent strength.

upon the degree of hydrolysis of the salt, and therefore lies in the alkaline region above the "neutral point."

Some typical graphs of titrations of alkaline solutions are given in Fig. 3.

Dibasic acids, or mixtures of a strong with a weak monobasic acid, give curves analogous to that for phosphoric acid, curve 3, Fig. 6. The advantage of the hydrogen electrode method in the determination of the acidity of dark-colored solutions is obvious. The curve for acetic acid, Fig. 2, is analogous to the titration graph of a specimen of very dark vinegar.

Study of Analytical Precipitations. Precipitation reactions are frequently caused by, or accompanied by, changes in hydrogen-ion concentration. In

certain instances it is possible to determine the end-points of volumetric precipitation reactions by means of the hydrogen electrode. Hildebrand and Harned [1] proved that a rapid and reasonably accurate determination of magnesia in the presence of lime, ferric oxide, etc., as in dolomite, could be made in this manner. A typical titration graph is given in Fig. 4. The distance, $a - b$, represents the amount of approximately normal alkali which was required to precipitate the magnesium hydroxide. The position of b was determined from the maximum of the rate of change of pH $\left(\text{max. value } \frac{\Delta pH}{\Delta V}\right)$, as suggested by Hostetter and Roberts.[2] Beyond b there is a second rather obscure inflection (not shown in Fig. 4) which corresponds to the end of the reaction:

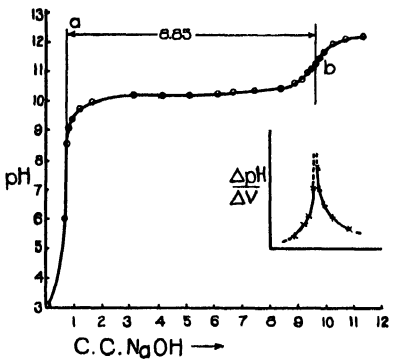


Fig. 4. Determination of Magnesia in Dolomite. Taken 1.0005 g. dolomite; Found 19.28%. A second determination gave 19.36%. Total time 4 hours. The average of several gravimetric determinations was 19.07%.

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl.$$

The sharp rise at the start of the titration corresponds to the neutralization of the excess of acid which was used to dissolve the dolomite, and the precipitation of ferric hydroxide.

It seems quite certain that an increasingly important use of the hydrogen electrode will consist in the study of the limiting ranges of pH which are suitable for analytical precipitations and separations. Hildebrand (*loc. cit.*) has pointed out its applicability for such purposes. Fales and Ware [3] have made an exhaustive study of the conditions for the precipitation of zinc as sulphide in this manner. They established pH, 2–3, as the optimum precipitation range, which they maintain by a buffer mixture (vide infra) of ammonium citrate, sulphate, formate, and formic acid. Relatively few investigations of this extremely useful type have thus far been made.

Buffer Solutions: It is almost impossible to prepare a solution of constant pH value by adding acid or alkali to pure water, since carbon dioxide from the air, or alkali from the glass vessels, rapidly alter the original value. On the other hand, buffer solutions, which are mixtures of acids or bases with an excess of alkali salt, possess the property of maintaining a stable hydrogen-ion concentration which is but little affected by additions of acid or alkali, or by

[1] Original Communication, *8th Internat. Congress Applied Chem.*, **1**, 217 (1912). See also Hildebrand, *loc. cit.*

[2] *J. Am. Chem. Soc.*, **41**, 1341 (1919).

[3] *J. Am. Chem. Soc.*, **41**, 487 (1919).

dilution. The resistance to change in hydrogen-ion concentration is called buffering, or buffer action.[1]

A comparison of curves (2) and (3), Fig. 5, with the dotted curves AC and AB will serve to illustrate the relative stability of buffer mixtures upon adding acid or alkali.

The approximate constancy of pH value upon dilution may be seen from the following observations of Michaelis (*loc. cit.*): The pH value of a mixture which was 0.1 N with respect to both acetic acid and sodium acetate was measured; the solution was then diluted five-fold and the measurements repeated.

$$\text{Original value } [H^+] = 2.42 \times 10^{-5} \text{ or } pH = 4.615;$$
$$\text{After dilution } [H^+] = 2.16 \times 10^{-5} \text{ or } pH = 4.665.$$

An approximate calculation of the hydrogen-ion concentration of a mixture of an alkali salt with either an acid or base may be made from the mass law expressions, equations (2) or (6). If we assume that the concentration of the undissociated acid is not appreciably different from the original acid concentration, and that the anion concentration is equal to the total salt concentration, equation (2) becomes:

$$[H^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}. \tag{22}$$

Equation (22) although serviceable in very dilute solutions fails to reproduce the electromotive force measurements in solutions which are far from concentrated (0.1 normal for example). If we correct for the degree of dissociation of the acid and introduce the degree of dissociation of the salt, α_{ba}, we have:

$$[H^+] = K_a \frac{[\text{Total Acid}] - [H^+]}{\alpha_{ba}[\text{Salt}] + [H^+]}, \tag{23}$$

and upon solving for $[H^+]$:

$$[H^+] = -\frac{\alpha_{ba}[\text{Salt}] + K_a}{2} + \sqrt{\frac{\alpha_{ba}[\text{Salt}] + K_a}{2} + K_a[\text{Acid}]}. \tag{24}$$

Equation (24) is a fairly useful approximation formula for dilute solutions of weak acids. Expressions which are analogous to (22–24) may be derived for hydroxyl-ion concentrations of mixtures of bases and salts.

The choice of suitable buffer mixtures may be made by an inspection of the titration curves, for, when $[\text{Acid}] = [\text{Salt}]$, $[H^+] = K_a$. Providing that we employ the usual concentration units, a mixture of salt and acid in equal proportions will give a buffer mixture whose $[H^+]$ is numerically equal to the dissociation constant of the acid. Conversely, the half titration point gives an approximate indication of the degree of dissociation of the acid.

[1] Clark (*loc. cit.*) states that the term buffer is derived from the German word Puffer (tampon).

The standard method for establishing the pH values of buffer mixtures consists in the use of the hydrogen electrode. Equation (21) with a correction for liquid junction potential, and for deviations of hydrogen pressure from one atmosphere, is used in calculating the hydrogen-ion concentration. In this manner a graded series of mixtures of known pH is prepared. Fig. 5 gives the graph of the relation between pH values and composition of some typical standard buffer mixtures. The dotted curves, AC and AB, represent respectively the calculated values for pH of 0 to 10.0 cc. of 0.1 normal hydrochloric acid or sodium hydroxide, after dilution in each case to 200 cc. with distilled water. Curves (1–5) are plotted from the data of Clark and Lubs,[1] (6) from work of Palitzsch,[2] and (7) of Walpole.[3] Sorensen [4] and others [5] have investigated a large number of buffer mixtures at various temperatures. These mixtures are essential to the indicator method of measuring hydrogen-ion concentration (vide infra). A few instances of buffer action in analytical precipitations and separations are:

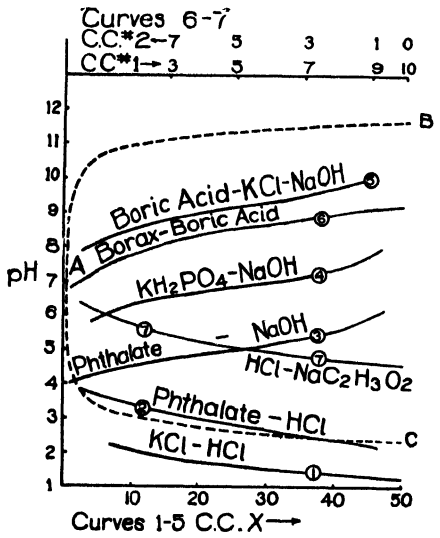


Fig. 5. Values of pH of Standard Buffer Mixtures

1. 50 cc. 0.2 N KCl plus X cc. 0.2 N HCl, diluted to 200 cc.
2. 50 cc. 0.2 M phthalate plus X cc. 0.2 N HCl, diluted to 200 cc.
3. 50 cc. 0.2 M phthalate plus X cc. 0.2 M NaOH, diluted to 200 cc.
4. 50 cc. 0.2 M KH_2PO_4 plus X cc. 0.2 M NaOH, diluted to 200 cc.
5. 50 cc. solution 0.2 M with respect to both H_3BO_3 and KCl plus X cc. M NaOH, diluted to 200 cc.
6. Mixtures of M/20 boric acid (No. 2) and M/5 solution of H_3BO_3 and NaCl (No. 1).
7. Mixtures of 20 cc. N sodium acetate (No. 2) and 1.0 N HCl (No. 1), diluted to 100 cc. Note. The scale for curves 6 and 7 is at the top of the figure.

Acetate—Acid mixtures in the separation of ferric, aluminium, or chromic ion from manganese, zinc, cobalt, or nickel. (Basic acetate method.) The separation of aluminium, titanium or zirconium from iron (ferrous).

Ammonium chloride—Ammonia mixtures in the separation of ferric iron, aluminium, etc., from calcium and magnesium. The separation of calcium from magnesium.

Ammonium phosphate—ammonium salt—Ammonia mixtures in the precipitation of magnesium, zinc, manganese, etc., as double phosphates.

[1] *J. Biol. Chem.*, **25**, 479 (1916).

[2] *Compt. rend. Carlsberg*, **11**, 199 (1916). See also Walbum, *Biochem. Z.*, **107**, 219 (1920).

[3] *J. Chem. Soc.*, **105**, 2501 (1914).

[4] *Biochem. Z.*, **21**, 131 (1909).

[5] For comprehensive review and discussion see Prideaux, The Theory and Use of Indicators, Chap. V (1917). D. Van Nostrand Co.; also Clark, *loc. cit.*, Chapter VI.

The use of these, and many other similar mixtures, has been developed empirically; exact knowledge of pH ranges which are permissible, although highly desirable, is still lacking in the majority of instances.

Indicators

The analytical determination of the equivalent point in a neutralization reaction is usually made with the aid of an organic substance which possesses one color in alkaline solution and a different color in acid solution. Such indicators are very feebly acidic or basic in character. Their action is the more sensitive the smaller the hydrogen-ion concentration range to which the visible color change is limited. This range should coincide as closely as possible with the hydrogen-ion concentration at the equivalent point, which in turn is determined by the degree of hydrolysis of the salt which is formed in the titration. Equations (16–18) and Table II will serve for the calculation of the transformation point as a function of strength of acid or base, and of concentration.

Ostwald [1] advanced the theory that indicator action is due to ionization, the undissociated molecule being of a color different from that of its ions. Phenol phthalein is weakly acidic in properties, and, according to the theory, may exist entirely—to all practical purposes—in the form of the undissociated molecule (which we will symbolize by HPh), in the presence of a very slight concentration of hydrogen ions. When the salt of the indicator is formed, however, extensive ionization occurs, and the pink anion (Ph^-) imparts its color to the solution. In the titration of a weak acid with sodium hydroxide the successive reactions are:

$$(a) \quad HA + Na^+ + OH^- = Na^+ + A^- + H_2O;$$
$$(b) \quad \underset{\text{Colorless}}{HPh} + Na^+ + OH^- = Na^+ + \underset{\text{Pink}}{Ph^-} + H_2O.$$

(a) is virtually complete before (b) commences, because of the slight concentration of HPh and its extremely small dissociation constant (K_a = about 2×10^{-10}).

The fact that phenol phthalein is unsuitable for the titration of weak bases, for example, ammonia, is explained by the hydrolysis of the salt of the indicator. At the equivalent point of the titration we would begin to have formed the salt NH_4Ph. Hydrolysis prevents the formation of a visible amount of Ph^- ions, thus:

$$NH_4^+ + Ph^- + H_2O \rightleftharpoons HPh + NH_4OH.$$

The solution remains colorless until a very considerable excess of ammonium hydroxide has been added.

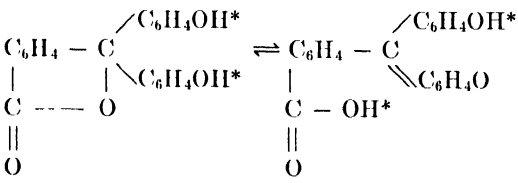
In an analogous manner we may explain the fact that a weakly basic indicator, for example, methyl orange, is suitable for the titration of a weak base,

[1] Ostwald, Scientific Foundations of Analytical Chemistry, 124. 2d Edition (1900). Macmillan & Co., London.

but valueless for the titration of a weak acid because of the hydrolysis of the indicator salt.

The titration of a concentrated solution of a strong acid with a strong base, or vice versa, may be made with any indicator whose color change occurs in the pH range 4-10, because hydrolysis is practically negligible (see Table V for dependence of pH range upon concentration).

Ostwald's theory is essentially in accord with the facts. It is now known, however, that the color change is due to intra-molecular rearrangement rather than to simple ionization. In general, indicator solutions consist of equilibrium mixtures of two, or more, tautomers, one of which prevails in a more acidic, the other in a more basic, range. There may be two or more color changes which occur at widely different pH ranges. (See Table IV, and thymol blue, Table VI.) The color change of phenol phthalein is ascribed to rearrangement in the sense of the reaction:



I. Colorless. II. Rose Colored.

The hydrogen atoms which are marked with asterisks have acidic properties. The color of (II) is ascribed to the chromophoric grouping, $= C_6H_4 = O$.[1]

Acree [2] and Noyes [3] have formulated mass action expressions for tautomeric equilibria. Noyes derives the following expressions for an acidic indicator having tautomers, HIn and HIn_1:

$$HIn \rightleftharpoons HIn_1 \quad \text{and} \quad (25)\ \frac{[HIn_1]}{[HIn]} = K_T;$$

$$(26)\ \frac{[H^+][In^-]}{[HIn]} = K_1 \quad \text{and} \quad (27)\ \frac{[H^+][In_1^-]}{[HIn_1]} = K_2.$$

Upon multiplying (27) by (25) and adding (26) to the product, and replacing HIn by its value:

$$\frac{[HIn] + [HIn_1]}{1 + K_T}$$

which is derived from (25), we have:

$$(28)\qquad \frac{[H^+]([In^-] + [In_1])}{[HIn] + [HIn_1]} = \frac{K_2K_T + K_1}{1 + K_T} = K_{IA}.$$

[1] For a complete discussion of the evidence see Thiel, *Ahrens Sammlung*, **16**, 353 and ff. (1911).

[2] *Am. Chem. J.*, **38**, 1 (1907); **39**, 529 (1908).

[3] *J. Am. Chem. Soc.*, **32**, 815 (1910).

If the indicator is a basic substance ($InOH \rightleftharpoons In_1OH$), the equilibrium expression is:

$$\frac{[OH^-]([In^+] + [In_1^+])}{[InOH] + [In_1OH]} = \frac{K_2K_T + K_1}{1 + K_T} = K_{IB}. \tag{28a}$$

Noyes calls K_{IA} or K_{IB} the "apparent dissociation constant." From an inspection of equations (28) and (28a) it is evident that the dominant factor in determining which tautomer shall prevail is the hydrogen-ion concentration. A strict mathematical treatment must include a consideration of the fact that many indicators are poly-basic or -acidic.[1] We may use equation (28) in the simpler form:

$$\frac{[H^+][In^-]}{[HIn]} = K_{IA},$$

wherein $[HIn]$ denotes the sum of the concentrations of substances in the acidic form and $[In^-]$ the sum of those in the basic. Therefore we may write:

$$[H^+] = K_{IA}\frac{[HIn]}{[In^-]} = K_{IA}\frac{(1-b)}{\alpha_{IS}b}. \tag{29a}$$

The quantity b is the concentration of the basic, and $(1 - b)$ of the acidic forms. α_{IS} is the degree of dissociation of the indicator salt. For a basic indicator:

$$[H^+] = \frac{K_w}{K_{IB}} = K_I\frac{\alpha_{IS}(1-b)}{b}, \tag{29b}$$

and if we regard the degree of dissociation of the indicator salt as unity, both equations (29a and b) are of the form:

$$[H^+] = K_I\frac{(1-b)}{b}. \tag{29}$$

The right-hand member is the "indicator function" of Noyes.

When the indicator is half transformed from acidic to basic form, we have the important relation $K_I = [H^+]$. This simple relation is of great importance in determining the hydrogen-ion concentration of solutions by the indicator method (colorimetric method, vide infra), or conversely in the determination of apparent dissociation constants of indicators. The latter determination is made as follows: Two tubes containing equal concentrations of indicator and in one case enough acid to produce the full acidic color, in the other an equivalent amount of base, are superposed. The resultant color is matched in a suitable colorimeter by an equivalent amount of indicator added to an appropriate buffer mixture. The buffer mixture tube and a tube of water are superposed in the same manner as those containing acidic and basic indicator solutions. In this manner the pH value of the point of half trans-

[1] Acree, *loc. cit.*, Rosenstein, *J. Am. Chem. Soc.*, **34**, 1117 (1912).

formation of the indicator is found; this value is numerically equal to the dissociation constant.

From the standpoint of the general theory of titrations the value of the indicator function is more important than that of the constant, since we titrate to the point of most clearly perceptible change, rather than to the point of half transformation, acidic to basic color. Various factors, such as color perception, color memory, and the relative brilliance of the two forms of indicator, need to be considered.

Table III contains a summary of indicator function values and suitable indicator concentrations. This table is derived from the results of Noyes, Bjerrum, and Prideaux (*loc. cit.*).

TABLE III

INDICATOR FUNCTIONS

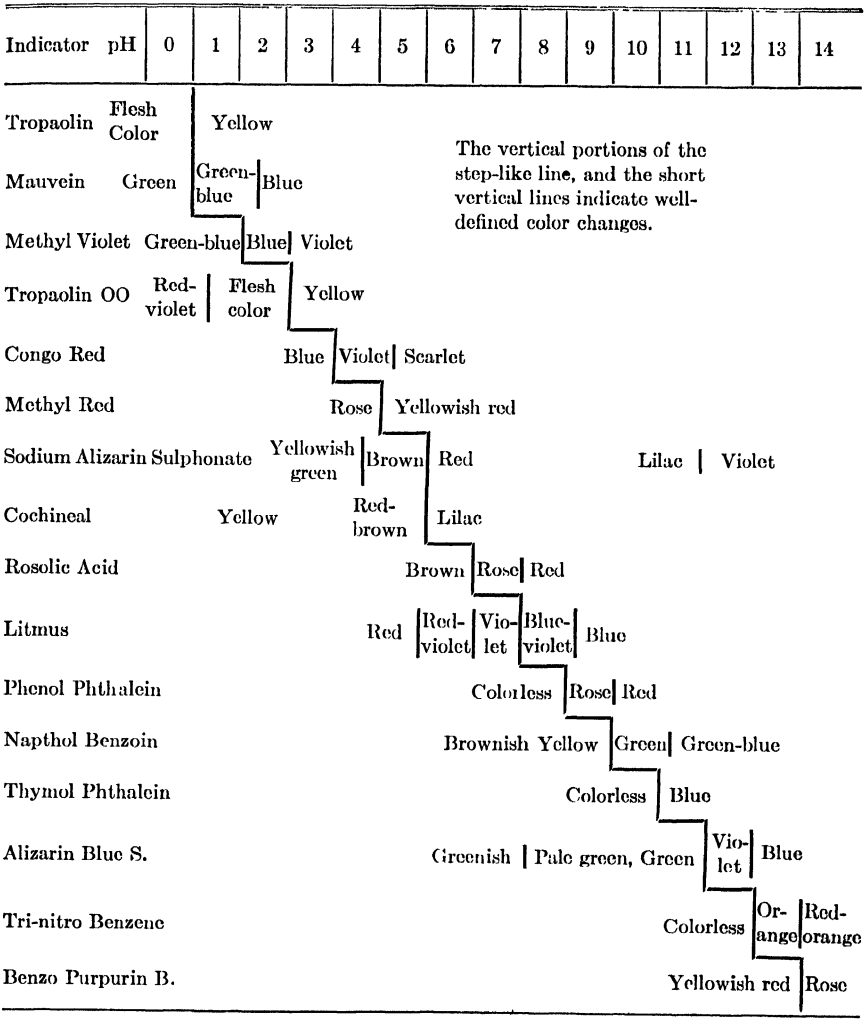
Indicator	Indicator Function		Indicator Concentration per 100 cc.	pH of the Trans. Point	Color Change
Dimethyl amino azo benzene	0.1 K_I	7×10^{-5}	0.1 cc. 1% sol.	4.0	First visible change, yellow-red
Methyl Orange	0.1 K_I	5×10^{-5}	0.1 cc. 1% sol.	4.3	First visible change, yellow-red
Methyl Red	0.3 K_I	3×10^{-6}	0.1 cc. 1% sol.	5.5	First visible change, yellow-red
Rosolic Acid	0.1 K_I	3×10^{-9}	1 cc. 1% sol.	6.5	Brownish to reddish
Phenol Phthalein	20 K_I	4×10^{-9}	0.7 cc. 1% sol.	8.0	Faint pink
	3 K_I	6×10^{-10}	0.4 cc. 1% sol.	9.0	Faint pink

These indicators serve for most of the titrations which are encountered in quantitative analysis. It is possible, however, to select an indicator whose color change occurs between any two desired pH units. Table IV contains a selection of such indicators from an extensive chart compiled by Thiel (*loc. cit.*).

Since the pH value of the equivalent point is determined by the hydrolysis of the salt in question, it is obvious that an indicator which is useful in concentrated solutions may be unsuited for the same titration in very dilute solution. Assuming that the error from this source alone should not be greater than one per cent, Bjerrum (*loc. cit.*) has calculated the permissible range of color transformation for varying dilutions as a function of the dissociation constant of the weaker constituent of the salt.

TABLE IV

COLOR TRANSFORMATION RANGES OF INDICATORS



Bjerrum points out that:

Only those intervals above the lines of the table are great enough to satisfy the demands of careful titration. Those within the lines may be located by electrometric or colorimetric methods. Those below the lines are so small that no known experimental method gives a satisfactory end-point. An inspection of the table shows that an acid of constant 10^{-6} could be titrated with the aid of a single indicator from N to 0.01 N solution (salt at end-point) since the

TABLE V

BJERRUM'S TABLE OF TITRATION INTERVALS FOR A DESIRED ACCURACY OF 1 PER CENT

K_a	Titration to N Salt		To 0.1 N Salt		To 0.01 N Salt		To 0.001 N Salt	
	p_T	p-interval	p_T	p-interval	p_T	p-interval	p_T	p-interval
∞	7	3–11	7	4–10	7	5–9	7	6–8
10^{-2}	8	5–11	7.52	5.04–10	7.15	5.14–9	7.02	6.04–8
10^{-4}	9	7–11	8.5	7–10	8.0	7–9	7.52	7.04–8.04
10^{-6}	10	9–11	9.5	8.96–10.04	9.0	8.8–9.2	8.5	8.43–8.57
10^{-8}	11	10.79–11.21	10.5	10.43–10.57	10.0	9.98–10.02	9.5	9.5 ±0.006
10^{-10}	12	11.98–12.02	11.5	11.5 ±0.006	10.98	10.98 ±0.002	10.43	10.43 ±0.0006
10^{-12}	12.98	12.98 ±0.002	12.47	12.47 ±0.0006	11.79	11.79 ±0.0002	10.96	10.96 ±0.00006

Note. The incomplete dissociation of the salt has not been taken into account. Hence the figures at the greater concentrations need a correction factor.

titration intervals have the pH range 9.0–9.2 in common. For the next lower constant (10^{-8}), a different indicator would have to be selected for each of the dilutions.

The considerations which we have discussed thus far apply at room temperatures, i.e., 18°–25° C. Increase in temperature affects K_w to a greater degree than the constants of the acid and of the indicator. Bjerrum's general theory of titration errors leads to the relation: $K_a > K_w \times 10^n$ in order that an acid may be titrated with an accuracy of one per cent. The value of n depends upon the dilution, being 8 for 0.02 N salt at the end-point. For this dilution at 20° C. an acid of constant greater than 10^{-6} could be titrated, while at 100° C. the constant would have to be greater than 0.6×10^{-4}. The transformation intervals of indicators are shifted to varying extents by rise in temperature to the boiling point. Titrations at or below room temperature are to be recommended whenever possible.

In practical instances, the presence of colloidal particles, filter fibers, or precipitates must be considered, since the tautomeric equilibrium may be disturbed by adsorption at the surfaces of these substances, one tautomer being more readily adsorbed than others. In colorimetric work this type of error is called the "protein error." When such an error is anticipated, the titration may be performed with several indicators of widely different chemical nature, which change color at about the same pH point. In many instances the indicator method must be abandoned in favor of the potentiometric or conductance method.

Salts exert an effect beyond that which would be expected from simple mass law considerations. Two solutions which give the same pH value with the hydrogen electrode when treated with the same amount of an indicator may give different shades of color. Since the hydrogen electrode is the standard,

the abnormality is ascribed to the indicator. In general, acidic indicators give positive salt errors and basic indicators give negative ones. For normal concentrations of alkali salts the error is of the order of 0.2–0.3 pH, and is not serious for the majority of titrations. (See Table V.) The indicators of Table III are among the least sensitive to salt action (except phenol phthalein).

The Hydrogen Electrode in Choice of Indicators: The significance of titration graphs for the choice of indicators is at once evident. The visible color change must fall in the pH region where the rate of change is a maximum $\left(\frac{\Delta pH}{\Delta V} = \text{max.}\right)$. The method of choice is indicated in Fig. 6, which gives titration curves of a number of acids together with a plot of the per cent transformation of several indicators from full alkaline to acid color as a function of pH. The horizontal shaded regions give the region of sharply visible change, which practically never coincides with the half transformation point. In order to check the correctness of the choice made in this manner, it is well to perform the potentiometric titration with the indicator present because of the uncertainty caused by salt effects, etc. (Hildebrand, *loc. cit.*).

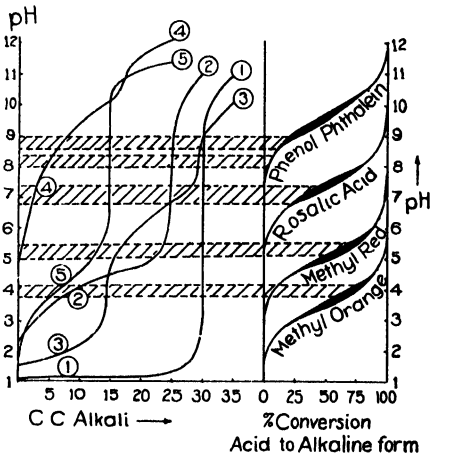


FIG. 6. Curve (1). 30 cc. of sulphuric acid titrated with sodium hydroxide of equivalent strength. (2) 25 cc. of acetic acid titrated with NaOH of equivalent normality. (3) Titration of 40 cc. of 0.0711 M phosphoric acid with 0.2 N NaOH. Davis, Oakes, and Salisbury, *Ind. Eng. Chem.*, **15**, 182 (1923). (4) and (5) Results of van Liempt, *Z. anorg. Chem.*, **111**, 151 (1920), curve (4) being the titration of boric acid alone, and curve (5) of an equivalent amount of boric acid plus 10 g. of mannite, the boric acid being thus converted into a relatively strong acid.

The Indicator Method of Measuring Hydrogen-Ion Concentration: The shaded portions of the indicator transformation curves at the right of Fig. 6 represent useful ranges of color change. By employing proper buffer mixtures, a succession of color standards is developed, each of which corresponds to a pH value slightly removed from the next, say by 0.2 pH. A volume of the unknown solution equal to that of the standard is treated with an equivalent amount of indicator. This solution will have a color between those of two of the standard comparison tubes. With suitable colorimetric technique the pH value may be accurately estimated to 0.1 pH.

Clark and Lubs [1] recommend the following carefully selected series of indicators as being especially adapted to the colorimetric method in connection with their series of standard buffer mixtures, curves 1–5, Fig. 5.

[1] *J. Bact.*, **2**, 1 (1917).

TABLE VI

CLARK AND LUBS SELECTED INDICATORS

Indicator	Concentration	Color Change	pH Range
Thymol sulphon phthalein (thymol blue) acid range	0.04%	Red–Yellow	1.2–2.8
Tetra bromosulphon phthalein (brom phenol blue)	0.04%	Yellow–Blue	3.0 4.6
Ortho carboxy benzene azo dimethyl aniline (methyl red)	0.02%	Red–Yellow	4.4–6.0
Di bromo ortho cresol sulphon phthalein (brom cresol purple)	0.04%	Yellow–Purple	5.2-6.8
Di bromo thymol sulphon phthalein (brom thymol blue)	0.04%	Yellow–Blue	6.0–7.6
Phenol sulphon phthalein (phenol red)	0.02%	Yellow–Red	6.8–8.4
Ortho cresol sulphon phthalein (cresol red)	0.02%	Yellow–Red	7.2–8.8
Thymol sulphon phthalein (thymol blue) alkaline range	0.04%	Yellow–Blue	8.0–9.6
Ortho cresol sulphon phthalein (cresol phthalein)	0.02%	Colorless–Red	8.2–9.8

POTENTIOMETRIC TITRATIONS[1]

We have briefly considered the analytical uses of the hydrogen electrode, which might be classified as: (1) The measurement of exact hydrogen-ion concentrations by the application of the concentration cell principle; and (2) The indication of end-points, or progress of reaction, in titration processes. In similar manner any other electrode which depends upon the reaction between an element and its ion might be capable of these uses. Electrodes other than the hydrogen electrode have occasionally been used in the solution of special processes of ion concentration measurement, e.g., the silver concentration cell in the measurement of the solubility of silver chloride.[2] From an analytical standpoint, however, the use of such electrodes in the determination of end-points is more important.

General Theory of Potentiometric Titrations: Every electrode process is an oxidation-reduction reaction, since it involves loss or gain of electrons by atoms or ions. For convenience we may divide electrode processes into three fairly distinct classes:

(*a*) The transfer of electrons between an element and its ion, e.g.:

$$Zn \rightleftharpoons Zn^{++} + 2\epsilon,$$
$$\tfrac{1}{2}H_2 \rightleftharpoons H^+ + \epsilon,$$
$$\tfrac{1}{2}Cl_2 + \epsilon \rightleftharpoons Cl^-.$$

The symbol ϵ, the electron equivalent, denotes the electronic charge associated with one gram equivalent. $\epsilon = -$ Faraday $= -$ 96,500 coulombs.

[1] Variously known as electrometric titrations, electrometry, electro-titrametric methods, etc.

[2] Goodwin, *Z. physik. Chem.*, **13**, 645 (1894).

(*b*) Processes which involve electronic transfer by increasing or decreasing the valence of an ion:

$$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon,$$
$$Fe(CN)_6^{----} \rightleftharpoons Fe(CN)_6^{---} + \epsilon,$$
$$MnO_4^{=} \rightleftharpoons MnO_4^{-} + \epsilon.$$

(*c*) Processes which involve electronic transfer with alteration in the oxygen content of the ion:

$$Mn^{++} + 4H_2O \rightleftharpoons MnO_4^{-} + 8H^{+} + 5\epsilon,$$
$$VO^{++} + 3H_2O \rightleftharpoons VO_4 \quad + 6H^{+} + \epsilon,$$
$$Cr^{+++} + 4H_2O \rightleftharpoons HCrO_4^{-} + 7H^{+} + 3\epsilon.$$

Expressions for the electrode potential due to each of these three types of processes have been derived by Nernst,[1] Peters,[2] and Crotogino,[3] respectively. Haber,[4] and Bancroft [5] have shown that the logical derivation of a common expression for all types of electrode processes is from the van't Hoff equation for the reaction isotherm, as follows: If the process is arranged to take place electrically, the maximum work $A = nFE$. The van't Hoff equation:

$$A = RTlnK\frac{p_1}{p_2} \tag{30}$$

then becomes:

$$E = \frac{RT}{nF} lnK\frac{p_1}{p_2}, \tag{31}$$

where p_1 refers to the partial pressures of the substances consumed, and p_2 to those of the substances produced. Therefore, if concentrations are proportional to partial pressures:

$$E = \frac{RT}{nF} lnK - \frac{RT}{nF} ln\frac{c_2}{c_1}. \tag{32}$$

The first term is obviously equal to the electromotive force, E_0, at unit concentration of all reacting substances. The equation may then be written:

$$E = E_0 - \frac{RT}{nF} ln\frac{c_2}{c_1}. \tag{33}$$

The sign of the electromotive force is positive when the reaction is written so that negative electricity flows from right to left across the phase boundaries

[1] *Z. physik. Chem.*, **4**, 129 (1889).
[2] *Z. physik. Chem.*, **26**, 193 (1898).
[3] *Z. anorg. Chem.*, **24**, 225 (1900).
[4] *Z. Elektrochem.*, **7**, 1046 (1901).
[5] *Trans. Am. Electrochem. Soc.*, **28**, 357 (1915).

within the cell.[1] For example, the equations for some typical processes are:

$$\text{Zn},\ \text{Zn}^{++} : \text{Zn} \rightleftharpoons \text{Zn}^{++} + 2\epsilon; \qquad E = {}_0E_{\text{Zn}} - \frac{RT}{2F} ln[\text{Zn}^{++}];$$

$$\text{Fe}^{+++},\ \text{Fe}^{++},\ \text{Pt} : \text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++} + \epsilon; \qquad E = {}_0E - \frac{RT}{F} ln \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}.$$

The value, ${}_0E$, for each process at normal concentrations of all reacting substances is referred to the value of the normal hydrogen electrode (= zero) as a standard.

If we represent the general oxidation-reduction reaction by:

$$aA + b'B' \rightleftharpoons a'A' + bB, \tag{34}$$

where A and B represent higher, and A' and B' lower, oxidation stages, we may divide the reaction into two opposed partial reactions with their characteristic electromotive force expressions:

$$(1)\quad aA + x\epsilon = a'A'; \qquad E_A = {}_0E_A + \frac{RT}{xF} ln \frac{[A']^{a'}}{[A]^a},$$

$$(2)\quad b'B' \rightleftharpoons bB + x\epsilon; \qquad E_B = {}_0E_B - \frac{RT}{xF} ln \frac{[B]^b}{[B']^{b'}}.$$

At equilibrium E_A equals E_B and therefore we have:

$$E_{\text{eq.}} = {}_0E_A + \frac{RT}{xF} ln \frac{[A']^{a'}}{[A]^a} = {}_0E_B - \frac{RT}{xF} ln \frac{[B]^b}{[B']^{b'}} \tag{35}$$

Whence

$${}_0E_B - {}_0E_A = \frac{RT}{xF} ln \frac{[A']^{a'}[B]^b}{[A]^a[B']^{b'}}.$$

The logarithmic expression on the right is the usual mass action constant of the reaction (34). Upon converting to common logarithms and substituting, for R and F, their values in electrical units, and assuming a temperature of 298° A, we have:

$${}_0E_B - {}_0E_A = \frac{0.059}{x} \log K. \tag{36}$$

This equation is of use in calculating equilibrium potentials and "breaks" in the potential curves at the end-point, as well as in the customary calculations of equilibrium constants from electromotive force data, etc.

The calculation of equilibrium potential is of interest because its value corresponds to the analytical end-point of the reaction. In simple special

[1] Lewis, *J. Am. Chem. Soc.*, **35**, 20 (1913), suggested this convention regarding sign.

cases the calculation is not difficult. Müller[1] gives the following methods of calculation for two cases which include the majority of analytical titrations.

Case 1. The coefficients of A and A', and also of B and B', are equal. $a = a'$; $b = b'$.

At the end-point of a given reaction the residual concentrations of A and B' are not unrelated, but stand in the ratio $a : b'$, since the two substances react in this ratio. In similar manner, A' and B will be present in the ratio $a' : b$. Therefore, at equilibrium,

$$(37)\quad \frac{[A]}{[B']} = \frac{a}{b'}, \qquad \text{and} \qquad (38)\quad \frac{[A']}{[B]} = \frac{a'}{b}.$$

Upon dividing (38) by (37) we have:

$$(39)\quad \frac{b[A']}{b'[A]} = \frac{a'[B]}{a[B']}$$

and hence:

$$\frac{[A']}{[A]} = \frac{[B]}{[B']}.$$

We may therefore write:

$$\left(\frac{[A']}{[A]}\right)^{a+b} = \left(\frac{[B]}{[B']}\right)^{a+b} = K, \qquad \text{or} \qquad (40)\quad \frac{[A']}{[A]} = \frac{[B]}{[B']} = \sqrt[a+b]{K}.$$

Substituting these values for these concentration ratios in (35), the equilibrium potential is:

$$(41)\quad E_{\text{eq.}} = {}_0E_A + \frac{0.059}{x}\frac{a}{a+b}\log K = {}_0E_B - \frac{0.059}{x}\frac{b}{a+b}\log K.$$

Upon substituting fo $\frac{0.059}{x}\log K$ its value from equation (36), we have for equilibrium potential in terms of normal potentials:

$$(42)\quad E_{\text{eq.}} = \frac{a\,{}_0E_B + b\,{}_0E_A}{a+b}.$$

With the aid of this equation we may calculate end-point potentials. These values are of considerable service in applying the first and second methods of the practical determination of end-points, which will be described (vide infra). As an illustration of the use of (42) let us calculate the end-point potential of the interaction between ferrous iron and bromate ion, assuming that the hydrogen-ion concentration is normal and the temperature is 25° C. The reaction is:

[1] Muller, Elektrometrische Massanalyse, 22 and ff. (1921). Th. Steinkopf, Dresden and Leipzig.

$$BrO_3^- + 6H^+ + 6Fe^{++} \rightleftharpoons Br^- + 3H_2O + 6Fe^{+++}$$

and the partial reactions are:

(1) $1(BrO_3^- + 6H^+) + 6\epsilon \rightleftharpoons 1(Br^- + 3H_2O)$; $\quad {}_0E_A = -1.420$ volts
$\quad a \qquad\qquad\qquad a'$ $\quad$ (Here $a = a' = 1$),

(2) $6Fe^{++} \rightleftharpoons 6Fe^{+++} + 6\epsilon$; $\quad {}_0E_B = -0.75$ volt
$\quad b' \qquad b$ $\quad$ $(b = b' = 6)$.

Therefore

$$E_{eq.} = \frac{(1 \times -0.75) + (6 \times -1.420)}{1 + 6} = -1.324 \text{ volts.}$$

This value is the internal E.M.F. of the cell. In practice a normal calomel cell is used as a reference standard. The external, or observed, E.M.F. of the cell: calomel electrode | solution | Pt electrode would then be $-1.324 + 0.284 = -1.040$ volts.

Case 2. Precipitation Reactions. The coefficients a and a' or b and b' are in general different. The product of the concentrations of A and B' is constant (solubility product).

$$[A]^a[B']^{b'} = k, \qquad \text{and} \qquad b'[A] = a[B'];$$

upon eliminating $[B']$ we have:

$$[A] = \sqrt[a+b']{\frac{k}{\left(\frac{b'}{a}\right)^{b'}}}. \tag{43}$$

In precipitation reactions we may so formulate the partial processes that $[A']$ and $[B]$ are constants whose values are included in those of ${}_0E_A$ and ${}_0E_B$. Substituting the value of $[A]$ from (43) in equation (35), the equilibrium expression is:

$$E_{eq.} = {}_0E_A - \frac{a}{a+b}\frac{0.059}{x} \log \frac{k}{\left(\frac{b'}{a}\right)^{b'}}. \tag{44}$$

For example in the precipitation reaction:

$$Ag^+ + I^- = AgI, \qquad k = 10^{-16} \text{ (solubility product).}$$

The partial reactions may be written:

(1) $Ag^+ + \epsilon \rightleftharpoons Ag$; $\quad {}_0E_{Ag} = -0.80$ volt.

(2) $Ag + I^- \rightleftharpoons AgI + \epsilon$; $\quad$ and $\quad a = a' = b = b' = x = 1$.

$$E_{eq.} = -0.80 - \tfrac{1}{2}\,0.059 \log 10^{-16} = -0.80 + 0.472 = -0.328v.$$

The value referred to the normal calomel electrode would be $-0.046v$. If we

substitute the value of $\frac{0.059}{x}\log K$ from (36) in equation (44), the latter becomes:

$$E_{eq.} = \frac{a_0E_B + b'_0E_A}{a + b'} - \frac{ab'}{a + b'}\frac{0.059}{x}\log\frac{b'}{a}. \tag{45}$$

(Note. In the derivation of equation (45) we assume that the partial reactions have been so written that the constant of the reaction is $1/k$, where k is the solubility product.)

The potential corresponding to the second partial reaction in the precipitation of silver iodide is 0.14 volt. Hence from

$$E_{eq.} = \frac{0.14 - 0.80}{2} - 0.00 = -0.330 \text{ volt.} \tag{45}$$

The discrepancy of 2 millivolts in the results of the two methods of calculation is due to slight inconsistency between the E.M.F. and solubility data.

From the normal potentials of the partial reactions it is possible to calculate the magnitude of the "break" in the potential curve near the end-point. Müller (loc. cit.) has developed the following expressions for the potential "break."

(*a*) *For Precipitation Reactions.*

$$\text{Potential "Break"} = {}_0E_A - {}_0E_B - \frac{0.059}{x}\log[A_{\text{initial}}]^a \times \text{Const.},$$

assuming that we always titrate to a final excess of B' whose value is expressed by the constant. Replacing $({}_0E_B - {}_0E_A)$ by its value from (36), and employing $\frac{1}{k}$ as the constant of the reaction, where k is the solubility product, we find:

$$\text{Potential "Break"} = -\frac{0.059}{x}\log\frac{1}{k} - \frac{0.059}{x}\log[A_{\text{init.}}]^a \times \text{Const.} \tag{46}$$

The numerical value of the potential rise or fall is greater the smaller the solubility product, and the greater the initial concentration of the ion to be precipitated.

(*b*) *Reaction in which no insoluble substance is involved.*

$$\text{Potential "Break"} = {}_0E_A - {}_0E_B = \frac{0.059}{x}\log\frac{1}{K} \tag{47}$$

if the "break" is reckoned from the point of half titration, i.e., $[B] = [B']$, to a constant slight excess of reagent.

Methods of Determining End-Points

Method 1. We have considered the most general method—that of determination of course of reaction—in the special case of neutralization reactions

whose progress was followed by the hydrogen electrode as an indicator electrode. The end-point was marked by an inflection in the curve. This method is perfectly general provided that an electrode can be found which will indicate correctly the relative changes in concentration of some one of the reactants. It is not necessary that the electrode process be truly reversible if we are interested merely in the determination of the equivalent point with ordinary analytical accuracy.

By way of illustration, let us consider the reaction between ferrous iron and potassium bichromate. Hildebrand (*loc. cit.*) presented a few results which brought out clearly the influence of acid concentration upon the sharpness of the potential "break" at the end-point. Curves 1 and 2, Fig. 7, illustrate the

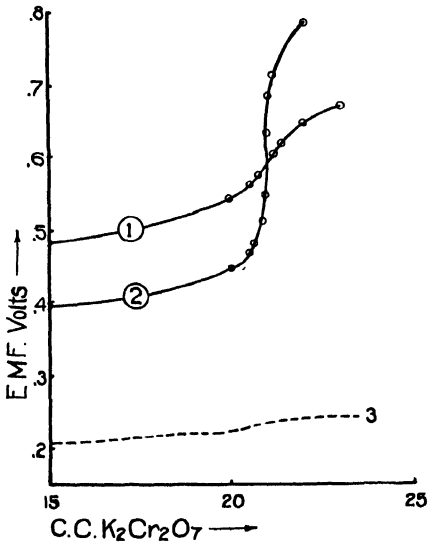


FIG. 7. (1) 20 cc. of approx. 0.1 N ferrous sulphate solution titrated with 0.1 N bichromate. About 5 per cent (by volume) of HCl, sp. gr. 1.2, present at start. (2) Repetition of (1) with 50 per cent of HCl present. (3) Curve obtained by Hostetter and Roberts upon substituting a palladium for the platinum electrode.

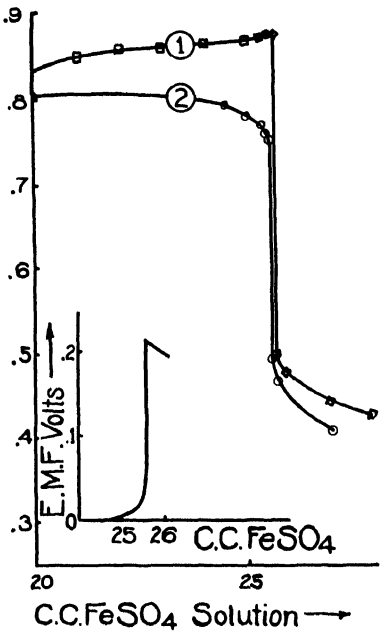


FIG. 8. 25 cc. 0.1 N bichromate solution titrated with approximately 0.1 N ferrous sulphate. For (1) the acid added was sulphuric, for (2) hydrochloric. Fig. 8A. Illustrates the nature of the end-point obtained by Willard and Fenwick in the reverse titration using a polarized platinum-tungsten electrode system.

influence of acid concentration. Hostetter and Roberts [1] have made a critical study of this method. Their results prove that it is one of the most accurate of volumetric processes.

[1] *J. Am. Chem. Soc.*, 41, 1337 (1919).

The reverse titration is of considerable interest. Forbes and Bartlett [1] found that there was an anomalous rise in potential shortly preceding the equivalent point, in the absence of chloride ion. In hydrochloric acid solution the anomalous rise does not occur; the curve is hardly a normal one, however. (Compare curves 1 and 2, Fig. 8.) Eppley and Vosburgh [2] have studied the method further. They found that the determination is strictly accurate over a limited range of acidity and bichromate concentration. The anomalous rise in potential is followed by a sudden violent drop at the end-point, which enables one to use a sudden deflection of a rather insensitive galvanometer as an indication of the end-point. Kelley and his collaborators [3] have shown that this procedure greatly simplifies the determination of chromium, vanadium, and manganese, in steels and ferro-alloys.

Method 2. A suitable indicator electrode and an electrode which duplicates the conditions at the end-point are joined by the solution under examination. The end-point is distinguished by a sudden fall of the potential difference to zero. A capillary electrometer, galvanometer, or even a sensitive voltmeter, serves to indicate the end-point. For instance, the cell:

Ag, solution of unknown $[Ag^+]$, KNO_3 saturated with AgI, Ag

would serve for the determination of silver with potassium iodide.

This method is obviously not limited to any particular type of reaction, and the apparatus is extremely simple. Its chief disadvantage lies in the necessity of preparing a different end-point electrode for each reaction.[4]

Method 2A. Pinkhoff (*loc. cit.*) has described what may be regarded as essentially a modification of the above method. An E.M.F. equal to that developed at the end-point ($E_{eq.}$) is opposed to that developed by the cell:

Pt, Unknown solution, Reference electrode.

A sudden reversal of polarity marks the end-point. A very simple potentiometer may be used. The chief disadvantage is the difficulty of compensating for the effect of foreign salts, variable concentrations, and temperature changes.

Method 3. In many precipitation reactions it is inconvenient or impracticable to use an electrode of the metal in question. This difficulty may be avoided in some instances by using a cathodically polarized platinum electrode in conjunction with a standard half cell.[5] Enough of the metal is deposited to give its characteristic electrode potential. The apparatus is indicated in Fig. 9. The rather complicated set-up and the unsatisfactory nature of the results detract from the value of the method. Under favorable conditions,

[1] *J. Am. Chem. Soc.*, **35**, 1527 (1913).

[2] *J. Am. Chem. Soc.*, **44** 2148 (1922).

[3] Kelley and Conant, *J. Am. Chem. Soc.*, **38**, 341 (1916); *J. Ind. Eng. Chem.*, **8**, 719 (1916). See also *J. Ind. Eng. Chem.*, **9**, 780 (1917); **10**, 19 (1918); **13**, 939, 1053 (1921).

[4] This procedure was developed principally by Pinkhoff, *Dissertation, Amsterdam* (1919), and by Treadwell, and Treadwell and Weiss, *Helv. Chim. Acta*, **2**, 672, 680 (1919).

[5] This device was proposed by Dutoit and von Weisse, *J. Chim. Phys.*, **9**, 578 (1911).

however, it enables one to determine a number of metals by successive precipitation with appropriate reagents.

The three methods which have been described depend more or less closely upon reversible electrode effects. Equations (36, 42, and 44–47) give reliable values only when the approach to true reversibility is very close. In every case where irreversible effects are in evidence, e.g., the titration of bichromate with ferrous iron, a special study must be made to determine whether the potential break corresponds to the equivalent point.

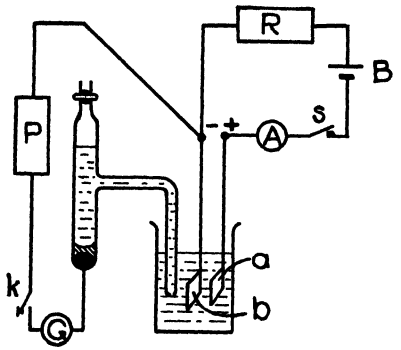


FIG. 9. Apparatus of Dutoit and von Weisse. *b*, cathodically polarized platinum electrode; *a*, auxiliary platinum electrode. The polarizing current was generally about 1×10^{-4} amp. maintained constant with the aid of battery, B, resistance, R, ammeter, A, and switch, S. P represents a potentiometer, G, a galvanometer.

The following method depends primarily upon certain transitory effects which appear at extremely small concentrations of active oxidizing or reducing agents.

Method 4. The Use of Polarized Bi-Metallic Electrode Systems. Hostetter and Roberts (*loc. cit.*) made the interesting observation that a palladium electrode in conjunction with a standard half cell did not give a rise in potential at the end-point of the titration of ferrous iron with bichromate. (Compare curves 1 and 2, Fig. 8.) They suggested that the palladium electrode might replace the usual calomel half cell with consequent simplification of apparatus. Willard and Fenwick [1] have made a thorough study of a large number of bi-metallic systems. Platinum with some other metal of its group (other than palladium), or with tungsten, furnished the most effective systems. The course of the titration curve is radically different from the usual curves with the platinum electrode-standard half cell system. There is zero difference of potential during most of the titration, or if tungsten is one of the metals, there is a gradual rise of about 50 millivolts; in every case the end-point is marked by an abrupt "break" of 100 to 200 millivolts. The "break" is generally limited to a range of about 0.5 cc. of 0.1 N titrating reagent. The break may be followed by rising, falling, or nearly stationary potential, depending upon the nature of the system.

The pre-treatment of the electrodes has a profound influence upon their behavior during the titration. Willard and Fenwick studied the polarization of one or both electrodes as a means of standardizing the pre-treatment. In highly acid solutions the anodic polarization of one electrode gave an improved break, as was predicted from theoretical considerations. Finally it was found that a system of two pure platinum wires of identical properties, the one

[1] *J. Am. Chem. Soc.*, **44**, 2504, 2516 (1922).

anodically, the other cathodically polarized with a current of about 0.5×10^{-5} amperes, gave the sharpest break of any system.

Willard and Fenwick explain the operation of the bi-metallic systems on the basis of the Nernst [1] hypothesis that oxidation and reduction potentials are due to definite pressures of oxygen or hydrogen with which the electrode is charged. This idea has been elaborated further by Peters[2] and Fredenhagen.[3] The phenomenon of the break or end-point difference in potential between two unattackable electrodes is explained by Willard and Fenwick as follows:

"When the concentration of oxygen ion or of hydrogen ion becomes vanishingly small, the osmotic pressure is too low for a saturation of the electrodes with the corresponding gas. The two elements receive the charge in accordance with the distribution law, and a difference of potential develops which is at its maximum with minimum concentration of the corresponding ion, and which falls rapidly as this ion concentration rises to a value in excess of that required for the saturation of both electrodes."

The character of the end-point with a polarized bi-metallic system is indicated in Fig. 8*A*.

The list of reactions which may be followed with analytical accuracy by the potentiometric method is large and is rapidly increasing. Table VII contains a list of some of the reactions which have been submitted to detailed study.

TABLE VII

REACTIONS WHICH GIVE ACCURATE END-POINTS BY THE POTENTIOMETRIC METHOD

(A) Precipitation Reactions [4]

Reaction	End-Point Method	Investigators
$Ag^+ + Br^- = \downarrow AgBr$	2	Behrend.
$Ag^+ + Cl^- = \downarrow AgCl$ } For either halogen or silver estimation.	3	Dutoit & von Weisse.
$Ag^+ + I^- = \downarrow AgI$	1	Lieblich.
$Ag^+ + CNS^- = \downarrow AgCNS$	1	Behrend.
$Ag^+ + K^+ + 2CN^- = KAg(CN)_2$ [5]	1	Treadwell (1).
	2	Müller et al. (1, 2, 3).
$2Ag^+ + S^{--} = \downarrow Ag_2S$	2	Treadwell (2).
	4	Willard & Fenwick (1).
$Hg^+ + Cl^- = \downarrow HgCl$		Behrend.
$Hg^+ + Br^- = \downarrow HgBr$		
$Mg^{++} + 2(OH)^- = \downarrow Mg(OH)_2$	1	Hildebrand & Harned.
$Zn^{++} + S^{--} = \downarrow ZnS$	2	Pinkhoff (1).
$3Zn^{++} + 2KFe(CN)_6^{---} = \downarrow Zn_3K_2[Fe(CN)_6]_2$ [6]	1	Hedrich.
		Knauth.
		Treadwell (2).
		von Bischowski.

[1] Nernst, "Theoretical Chemistry," p. 762, 6th Edition (1911), Macmillan & Co., London.

[2] *Loc. cit.*

[3] *Z. anorg. Chem.*, **29**, 396 (1902).

[4] Some instances of stable complex formation are included.

[5] This reaction has been used for the determination of Ni, Co, or Zn; a known excess of potassium cyanide is added. Back titration with silver nitrate gives a measure of the excess.

[6] The addition of a small amount of ferricyanide enables the end-point to be determined with an oxidation potential set-up, the partial reactions being:

(*A*) $3Zn^{++} + 2KFe(CN)_6^{---} + 2\epsilon \rightleftharpoons K_2Zn_3[Fe(CN)_6]_2$

(*B*) $2KFe(CN)_6^{----} \rightleftharpoons 2KFe(CN)_6^{---} + 2\epsilon$

Copper and cadmium enter into analogous reactions.
$2Pb^{++} + Fe(CN)_6^{=} = \downarrow Pb_2Fe(CN)_6$ Müller & Gabler.
(Lead and zinc may be determined in the same solution.)

(B) Oxidation-Reduction Reactions

Halogens. The problem of the potentiometric determination of the halogens has been subjected to a considerable amount of study. Total halogen is determined by precipitation with silver ion.

Reaction	End-Point Method	Investigators
Iodide in presence of Cl^- or Br^- is oxidized by an excess of hypobromite. The excess is estimated with standard arsenite solution.	1 or 4	Willard & Fenwick (2).
Selective oxidation of bromide: $2MnO_4^- + 16H^+ + 5Br^- + 5CN^- = 2Mn^{++} + 8H_2O + 5BrCN$ (Iodide enters into a similar reaction.)	1	Willard & Fenwick (2).
Oxidation of Iodide Ion:		
$BrO_3^- + 6H^+ + 6I^- = Br^- + 3H_2O + 3I_2$	1	Kolthoff (1); Hendrixson (1).
$2HCrO_4^- + 14H^+ + 6I^- = 2Cr^{+++} + 8H_2O + 3I_2$	1	Hendrixson (1).
$IO_3^- + 6H^+ + 5I^- = 3I_2 + 3H_2O$	1	Kolthoff (1).
$2MnO_4^- + 16H^+ + 10I^- = 2Mn^{++} + 8H_2O + 5I_2$	1	Crotogino; Hendrixson (1). Kolthoff (2).
Various Reactions.		
$2Cu^{++} + 4I^- = 2CuI + I_2$	1	Osterheld & Honegger.
$I_2 + 2S_2O_3^{=} = S_4O_6^{=} + 2I^-$	1 or 2*A*	
$BrO_3^- + 6H^+ + 3Sb^{+++} = Br^- + 3H_2O + 3Sb^{+++}$	2*A*	Zintl & Wattenberg (1).
$BrO_3^- + 6H^+ + 3As^{+++} = Br^- + 3H_2O + 3As^{+++}$		
$BrO_3^- + 6H^+ + 3Tl^+ = Br^- + 3H_2O + 3Tl^{+++}$		
$BrO_3^- + 6H^+ + 6Fe^{++} = Br^- + 3H_2O + 6Fe^{+++}$	1	Kolthoff (2).

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Kelley & Conant, *loc. cit.*
Knauth, *Dissertation, Dresden* (1915).
Kolthoff, (1) *Rec. trav. chim.*, **39**, 208 (1920). (2) *Chem. Weekbl.*, **16**, 450 (1919). (3) *Rec. trav. chim.*, **40**, 532 (1921). (4) *Ibid.*, **41**, 343 (1922). (5) *Ibid.*, **42**, 186 (1923). See also Biilman, *J. Soc. Leather Trades Chem.*, **5**, 27 (1921); also Sörensen et al., *Ann. chim.*, **16**, 283 (1921).
Lieblich, *Dissertation, Dresden* (1920).
(1) Müller & Lauterbach, *Z. anal. Chem.*, **61**, 457 (1922).
(2) Müller & Lauterbach, *ibid.*, **62**, 23 (1923).

0.5 to 0.8 per cent with a conductance set of moderate precision (0.2 per cent). By using a weight burette, an accurately controlled thermostat, and a more sensitive conductivity set, a much higher order of accuracy is obtainable.

In general, if conductance values, or, more simply, bridge readings, with a constant comparison resistance, are plotted as ordinates, against cc. of reagent as abscissæ, we obtain a titration graph which consists of two intersecting straight lines. The abscissa of the point of intersection is the equivalent point.

The accuracy of the method is greater the more acute the angle of intersection, and the more closely the points of the graph lie upon straight lines. If the lines are to be straight, it is theoretically necessary that the volume of the solution shall not change during the titration. This condition is regarded as being satisfied in practice if the total volume of reagent does not exceed one to two per cent of that of the unknown solution. The reagent should therefore be as concentrated, and the solution as dilute as feasible.

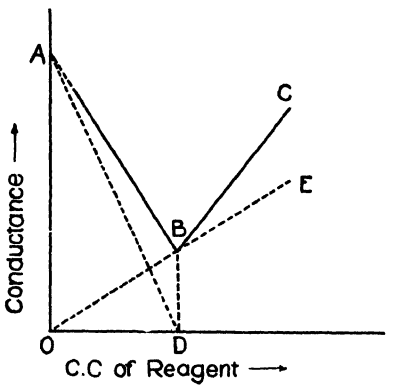


FIG. 11. Titration of a Strong Acid with a Strong Base

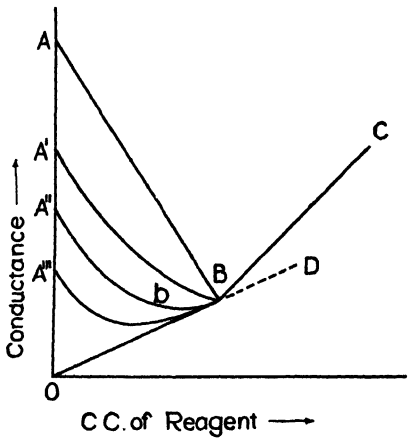


FIG. 12. Titration of Acids of Various Strengths, with a Strong Base

Other important factors which affect the accuracy of the method are:

(*a*) The degree of electrolytic dissociation of the various substances; (*b*) The ionic conductances; (*c*) Hydrolytic action; and (*d*) The solubility of precipitates, or the stability of complexes. We shall consider the influence of these factors upon the more important individual types of conductance determinations.

Thesis, Lausanne (1908). Dutoit, *Bull. Soc. Chim.*, **7** (1910). An address of 39 pp. which gives a resumé of his work upon neutralization, displacement, and precipitation reactions. A brief bibliography is included. See also Dutoit, *J. Chim. Phys.*, **8**, 12 (1910); Dutoit and Mojiu, *ibid.*, **8**, 27 (1910). Thiel and Roemer, *Z. physik. Chem.*, **63**, 711 (1908). Van Suchtelen and Itano, *J. Am. Chem. Soc.*, **36**, 1793 (1914). Harned, *ibid.*, **39**, 252 (1917).

[3] *Z. anorg. Chem.*, **111**, 1, 28, 97 (1920); **112**, 155, 165, 172, 187, 196 (1921). *Z. analyt. Chem.*, **61**, 171, 229, 332, 369, 433 (1922); **62**, 1, 97, 161, 209 (1923).

(A) Neutralization Reactions: (*a*) *Titration of a Strong Base with a Strong Acid*, or vice versa. The graph of such a titration consists of two straight lines intersecting at an acute angle, Fig. 11. Accurate results may be obtained even at extreme dilutions. The line AB represents the progress of the neutralization; it is a composite of OB, which represents the conductance of the salt formed, and AD which is that of the acid. The line BC represents the conductance due to salt formed plus that due to excess of reagent.

Other things being equal, the accuracy is greater the lower the conductance of the cation of the base.

(*b*) *Titration of a Moderately Strong or Weak Acid with a Strong Base.* A series of neutralization curves is represented in Fig. 12. $A'B$ represents the titration of a moderately strong acid with a strong base. As we deal with progressively weaker acids the curve tends finally to approach the salt line ($A''B$, $A'''B$, and finally OB); extremely weak acids give titration graphs of the form OBC. In general there is a minimum in the curves for moderately strong acids (as at b, curve $A''B$).

Upon the assumption that the equivalent point may be accurately determined, i.e., that the neutralization curve coincides with the salt line, if the conductance due to acid is not more than one per cent of that due to salt at 75 per cent neutralization, Kolthoff finds that the titration of a moderately strong acid gives accurate results:

In 0.1 N solution if the dissociation constant, K_a, is less than 5×10^{-4},
In 0.01 N " " " " " " " " " 5×10^{-5},
In 0.001 N " " " " " " " " " 5×10^{-6}.

For the calculation, equation (2) is written in the form:

$$\frac{x(a+x)}{b-(a+x)} = K_a \times 10^3,$$

where x is hydrogen-ion concentration, b the original acid concentration, and a that of alkali added, all expressed in milli-equivalents per liter. If we assume that:

$$\Lambda_{H^+} + \Lambda_{A'} = 350, \quad \text{and} \quad \Lambda_{B^+} + \Lambda_{A^-} = 80,$$

then:

$$x = \frac{1}{100} \times \frac{80}{350} \times 75 = 0.172,$$

$b = 100$, and $a = 75$, whence:

$$K_a = \frac{0.172(75 + 0.172)}{10^3[100 - (75 + 0.172)]} = 5 \times 10^{-4}.$$

In a similar manner the lower limit of the dissociation constant of a weak acid may be calculated. In this instance, the hydrolysis of the salt which is formed is the determining factor. Kolthoff assumed that the neutralization

curve would coincide with the salt line, or would at all events be straight from the point of three-fourths neutralization to the end-point, if, at this instant, the conductance of hydroxyl ion due to hydrolysis did not exceed 1 per cent of the total. He calculated that for an 0.1 N solution K_a must be equal to or greater than 2×10^{-10}, and for an 0.01 N solution, equal to or greater than 2×10^{-9}. (Calculation made by using equations (13*a* and *b*), assuming $\Lambda_{A^-} = 35$, $\Lambda_{OH^-} = 174$, and that:

$$[OH] = \frac{1}{100} \times \frac{35}{174} \times [\text{salt conc'n}].)$$

Accurate results were obtained in the titration of 0.1 N boric acid, phenol, hexamethylene tetra-amine, etc., whose dissociation constants lie between 10^{-10} and 10^{-9}. With 0.01 N solutions, however, the accuracy is scarcely satisfactory.

Considerations similar to the above are applicable, *mutatis mutandis*, to the titration of moderately strong or weak bases with strong acids.

(*c*) *Titration of a Weak Acid with a Weak Base*, or vice versa. Hydrolysis is a factor of much less significance in this instance than in the preceding case. Upon the assumption that 1 per cent hydrolysis at 90 per cent neutralization will not interfere with the attainment of analytical accuracy, Kolthoff derives 3×10^{-6} as the minimum values for dissociation constants of both acid and base. (Calculated with the substitution of appropriate numerical values in equation (19).) His results in the titration of acetic and oxalic acids with ammonia are presented in Fig. 13. It will be noted that oxalic acid, in common with the majority of dibasic acids, gives a graph which is precisely like that of a mixture of a fairly strong with a much weaker acid.

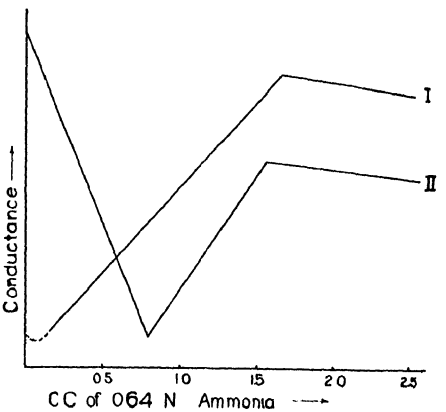


FIG. 13. Results of Kolthoff. Curve I. Titration of 10 cc. 0.107 N acetic acid. Curve II. Titration of 10 cc. 0.100 N oxalic acid.

(*d*) *Displacement Reactions.* These reactions involve the question of the partition of an acid between two bases, or vice versa. We may determine the end-point of the displacement of ammonia from ammonium chloride by sodium hydroxide, of acetic acid from sodium acetate by hydrochloric acid, of pyridine from pyridine acetate by sodium hydroxide, etc. The titration graphs are analogous to those which represent the titration of very weak acids with strong bases.

The special advantages of the conductance method applied to neutralization and displacement reactions depend upon the applicability of the method to

the examination of extremely dilute solutions, and especially to the determination of substances whose degree of dissociation is extremely slight. The displacement reactions are of especial significance in the examination of urine and other physiological liquids. The advantage of the conductance method in the analysis of colored solutions is obvious.

(B) Precipitation Reactions: The conductance method is particularly suitable for the determination of the end-points of analytical precipitations, since a degree of solubility which would vitiate ordinary gravimetric results is often without influence upon the accuracy of this method. Let us consider the general precipitation reaction: $BA + CD = \downarrow BD + CA$.

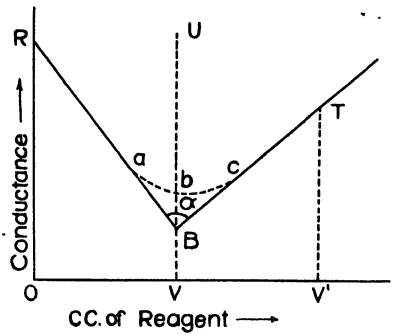


FIG. 14. Graph of a Precipitation Reaction.

Suppose that 100 cc. of an 0.001 N solution of BA are titrated with a normal solution of CD. The graph is represented in Fig. 14. Assume that the volume of the solution is not changed (in reality it is 100.1 cc. at the equivalent point). Then let Λ_B, Λ_A, Λ_C, and Λ_D represent the ionic conductances. The ordinate OR (Fig. 14) represents the original conductance and is equal to $0.001(\Lambda_B + \Lambda_A)$. Assuming a completely insoluble precipitate, the ordinate VB is equal to $0.001(\Lambda_C + \Lambda_A)$. Similarly $V'T$ is equal to $0.001(2\Lambda_C + \Lambda_A + \Lambda_D)$. The tangent of the angle, α, may be derived from those of angles RBU and UBT. If we let $OV = VV' = M$, and the normality of the original solution N, we have:

$$\tan \alpha = \frac{-(\Lambda_B + \Lambda_D)M}{M^2 + N^2(\Lambda_C - \Lambda_B)(\Lambda_C + \Lambda_D)}.$$

From this relation it follows that:

1. The angle α, and hence the sharpness of the end-point, is independent of the nature of the anion A.
2. α decreases as Λ_D increases.
3. α increases as Λ_C increases.
4. α increases as M increases.

Dutoit derived the above relationships, and from them a number of practical rules, which Kolthoff has studied, and somewhat modified, as follows:

1. The nature of the original anion is almost without influence when a cation is to be precipitated, and vice versa. On account of their great mobilities hydrogen and hydroxyl ions must be excepted. It is a matter of indifference whether we precipitate barium as sulphate from a solution of chloride or acetate. A solution of barium hydroxide would not be satisfactory.

2. The sharpness of the end-point will be greater in proportion as the conductance of that ion of the reagent which enters into the precipitate is greater.

For example, it is possible to use a sulphate, carbonate, or chromate, to precipitate barium ion. Since the mobility of the sulphate ion is highest, its use is most satisfactory.

3. The smaller the conductance of that ion of the reagent which does not enter the precipitate, the greater will be the accuracy of the method. In general, cations are best precipitated by adding lithium salts, and anions by adding acetates. It is not possible to obtain a satisfactory conductance determination of barium by adding sulphuric acid. Lithium sulphate, however, gives excellent results.

Harned (*loc. cit.*) has developed what may be regarded as a logical extension of this rule. He chooses conditions so that two insoluble substances are formed. Thus, both ions of magnesium and various other sulphates are precipitated by barium hydroxide. This method gives a very rapid and excellent determination of magnesium in the presence of calcium.

4. The reagent must be at least ten times as concentrated as the unknown solution. The latter should be at least as dilute as N/40. When the solubility of the precipitate is slight enough, excellent results are obtained in 0.001 N solutions. A good average working range is 0.01 to 0.02 N.

5. Foreign salts which do not react with the precipitating solution do not affect the end-point even when present in rather large excess over the concentration of the ion which is to be precipitated.

The operation of the above rules is considerably modified in practice by the following disturbing influences:

Solubility of Precipitates. The effect of solubility is to give a rounded portion of the curve near the equivalent point. The dotted line *abc*, Fig. 14, indicates the effect of solubility of precipitate. Providing that a suitable distance of both curves *Rab* and *bcT* is straight, an accurate determination of the end-point is obtained by producing these straight portions until they intersect. The distance *Bb* is a measure of the solubility of the precipitate. There is a fairly definite relationship between order of solubility of precipitate and degree of dilution, which must be satisfied if the results are to be accurate. Dutoit states that the conductance of the soluble product of the reaction must be 50 to 100 times that of the ions of the precipitate. Kolthoff derives the relation as follows:

Assuming that the results are satisfactory, if the conductance due to precipitate is not greater than 1 per cent of the total when half of the stoichiometrical amount of CD has been added, for an 0.1 N solution of AB, since $[D] = 5 \times 10^{-4}$, and $[A] = 0.05 \times (5 \times 10^{-2})$, the solubility product must be equal to or less than 2.5×10^{-5}. The solubility of the precipitate must be less than 0.005 N approximately. For a 0.001 N solution, the solubility could not exceed 0.00005 N. This indicates that silver or chloride ion may be determined by the conductance method in 0.001 N solution since the solubility of AgCl is 1.05×10^{-5} at 20° C.

Adsorption. The effect of true adsorption is to give irregular conductance values. The approximate point of inflection does not correspond to the true

equivalent point. This effect is not to be confused with a temporary retention of reagent by the precipitate. In this latter case the conductance increases to a definite maximum in 2 to 3 minutes; the results are accurate, although the process is tedious. Where true adsorption occurs accurate results cannot be obtained.

Inconstancy of Composition of Precipitate. Obviously such a factor renders the method useless. Harned found that copper could not be determined with sodium hydroxide since the end-point varied with the dilution, etc., the general average end-point being at about six-sevenths of the theoretical quantity of alkali. In general precipitations with alkali hydroxides are not satisfactory.

Slow Precipitation. This tendency is connected with the phenomena of colloidal behavior. In general the presence of acid during the precipitation of multivalent cations, or of alkali in case of anions, increases the rate of precipitation.

The addition of alcohol or of other organic solvents modifies solubility, conductance, and rate of precipitation. In many instances such an addition makes the application of the conductance method possible.

Formation of Undissociated Substances. When a slightly dissociated compound is formed in a reaction, the end-point may be determined by the conductance method. Considerations similar to those relating solubility of precipitates to degree of dilution determine the limitations in this case. Mercuric perchlorate reacts with many organic acids to give slightly dissociated mercuric compounds. For example, acetates or formates may be accurately determined in 0.1 N solution by this method.

Electrometric Recording and Control of Reactions

It is obviously desirable to have a continuous automatic record of the progress of a reaction, or to be able to control a process by automatic additions of appropriate reagents. Electrometric methods are highly satisfactory for such purposes. The point of balance of a potentiometer or Wheatstone bridge may be found automatically, and continuously recorded upon a chart. An alternate method is to allow the system to remain unbalanced and to record or indicate the degree to which it is unbalanced as a function of progress to the reaction. Automatic instruments of the types which have been developed for recording temperatures, as indicated by thermo-couples, serve equally well in recording acidity, salt concentration, and the like. The recording instrument may be made to operate valves for addition of reagents, or alarm signals, at definite limits of pH or conductance.[1]

A novel suggestion for the continuous indication of hydrogen-ion concentration has been made by Goode, who employs a three-electrode electron tube, or "audion" tube. The device whose essential features are indicated in Fig. 15

[1] Keeler, *J. Ind. Eng. Chem.*, **14**, 395 (1922); *Power*, **55**, 126, 768 (1922), has described some of the applications of automatic potential and conductance methods. Rideal, *Chem. Age (London)*, **5**, 232 (1921), has outlined the possibilities of electrometric control in chemical industries.

may be regarded as a direct reading sensitive voltmeter which draws no current from the titration cell; the readings may therefore be made continuously.[1] The plate current, I_p, is regarded by Goode as being the sum of a current, I_0, which is constant for a given tube under properly regulated conditions, and the current $(I_p - I_0)$, which is a function of the grid potential, and hence of the hydrogen electrode potential. If the effect of I_0 is balanced out by an opposed current, the galvanometer, G, gives direct readings of $(I_p - I_0)$ and hence a measure of pH. The current I_0 is balanced by adjustment of the resistance, R', so that the galvanometer reading is zero. By proper adjustment, the galvanometer scale may be calibrated to give pH readings directly.

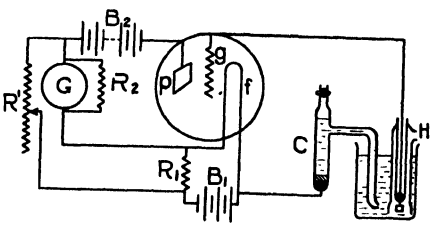


FIG. 15. Goode's Continuous Reading Electro-Titration Apparatus. C, calomel cell, H, hydrogen electrode, B_1, six volt battery, B_2, 22.5 volt battery, R_1, resistance, about 0.6 ohm. R_2, 25 ohms. R', variable high resistance. G, galvanometer. p, f, g, plate, filament, and grid of electron tube.

With this device, titration curves were obtained which were in all respects similar to those of Figs. 2–4.

Clark (*op. cit.*) suggests that the electron tube may be used as an amplifier in causing electrode potential differences to control industrial processes.

The electrometric method is by no means limited to ordinary solutions; many applications of the method have been made to the analysis and control of the composition of gas mixtures. Naturally, indirect methods are employed, although Rideal (*loc. cit.*) has suggested the direct analysis of certain gas mixtures by applying them to one electrode of a gas concentration cell, the other electrode being surrounded by a pure gas, or a mixture of known composition. The potential difference would then measure directly the partial pressure of the active component.

Electrolytic conductivity measurement has been applied to the analysis of gaseous mixtures. The method consists in the absorption of a component of the mixture by a suitable solution whose variation in electrical conductance is then a measure of the per cent of the substance in the mixture.[2] For example, the amount of carbon dioxide may be determined by the alteration in conductance of barium hydroxide or ammonia solutions which results upon absorption of the carbon dioxide. The method may be utilized in the determination of a number of components of a mixture either by using a series of reagents or by alternating conductance measurements and preferential catalytic combustion of some substance. For example, carbon monoxide, dioxide, and methane might be determined in a mixture by the latter process.

[1] Goode, *J. Am. Chem. Soc.*, **44**, 26 (1922). Subsequently, Calhane and Cushing, *Ind. Eng. Chem.*, **15**, 1118 (1923), have applied the method to a precipitation reaction.

[2] Taylor, G. B., and Taylor, H. S., *J. Ind. Eng. Chem.*, **14**, 1008 (1922). A constant ratio of gas mixture and solution flow is necessary to the success of the method. An ingenious mechanical device for maintaining this ratio is described.

Electrical thermometry has been applied in various ways to the analysis of gas mixtures. Lamb and Larson [1] have described two electro-thermometric methods for the determination of carbon monoxide in air: (*a*) The mixture is first passed over a platinum wire heated to redness; part of the carbon monoxide is burned, heating the wire further. The residual carbon monoxide is removed by hot copper oxide, and the gas is brought to its original temperature; it is then passed over a platinum wire which is identical in properties with the first, and heated by the same current. The resultant relative change in the resistance of the two wires is calibrated in terms of per cent carbon monoxide by means of a series of mixtures of known composition. (*b*) The electrically measured rise in the temperature of a catalytic mass of platinized platinum, at whose surface the carbon monoxide burns completely, is calibrated in terms of per cent carbon monoxide. Obviously these methods are capable of numerous further applications.

The Thermal Conductance Method: A very general method for the continuous analysis of gaseous mixtures depends upon the fact that the thermal conductivities of the individual gases differ widely. When an electrically heated wire is surrounded with a gas flowing in a tube whose walls are at constant temperature, the dissipation of heat, and hence the equilibrium temperature of the wire, depends primarily upon the thermal conductivity of the gas, if conditions are properly chosen. The resistance of the wire is a function of the temperature, and hence of the composition of the mixture.

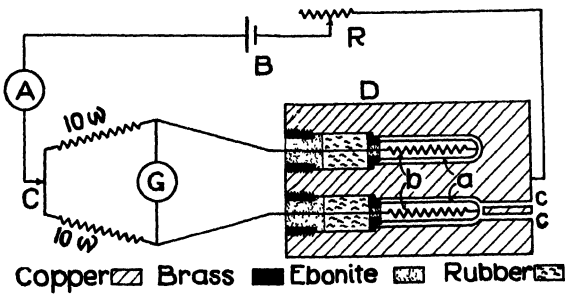


FIG. 16. The Shakespear Katharometer. B, battery, R, resistance, A, ammeter, C, bridge contact, G, galvanometer. a, a, copper wires which support the platinum wires b, b and bring them into electrical contact with the copper block, D. c, c, openings for gas to be analyzed. Size of block D, $1\frac{1}{16}$ x $1\frac{3}{4}$ inches.

In practice a differential method is employed. Two platinum wires of as nearly as possible identical properties form two of the arms of a Wheatstone bridge. The wires are placed axially in two similar tubes in a metal block, which is kept at constant temperature. One wire is surrounded with the unknown mixture, the other with a reference gas, or with the mixture after the component to be determined has been removed. A previous calibration of the apparatus with mixtures of known composition enables one to read the

[1] *J. Am. Chem. Soc.*, 41, 1908 (1919).

CHAPTER XIV

REACTION VELOCITY IN HOMOGENEOUS SYSTEMS

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If we add a solution of iodine to a solution of sodium thiosulfate, the reaction which takes place is practically instantaneous even in the most dilute solution, and this reaction is typical of a whole host of others occurring in inorganic chemistry; occasionally in this field we find a reaction such as the catalytic decomposition of hydrogen peroxide by the iodide ion [1] which proceeds at a measurable rate; but, the great bulk of the reactions in inorganic chemistry proceed at a rate too fast to be measured. The rate of such reactions is determined by the rate at which the substances can be mixed, since the mixing is followed by a practically instantaneous combination. On the other hand, we find that the great bulk of the reactions occurring in organic chemistry proceed at a measurable rate; if we add a solution of methyl iodide to a solution of sodium thiosulfate, we find that, instead of occurring instantaneously as in the iodine-thiosulfate reaction, it takes several hours to go to completion. We can therefore make an empirical generalization by saying that reactions between the polar or ionized compounds of inorganic chemistry are usually instantaneous, but that, when one or more of the compounds is a non-polar substance, the reaction proceeds at a slow measurable rate; there are relatively few exceptions to this rule.

We may make a second empirical generalization by saying that most of these "slow" reactions are catalytic in character, so that the study of reaction velocity may almost be said to be a study of catalysis; there are a few exceptions to this rule but it is possible that such reactions may prove ultimately to be catalytic in character. Most of the studies of reaction velocity have been made with the reacting substances in dilute solution; obviously this simplifies the problem, because we can apply the various laws that hold in dilute solution and which would not apply in concentrated solution or with the pure substances. There have been some measurements made of the reaction velocity in gaseous mixtures since, in some cases, such as the combination of nitric oxide and oxygen, the reaction proceeds with measurable velocity; however, in nearly all such cases there is the suspicion that the walls of the containing vessel affect the reaction, in which case it would really be heterogeneous; consequently reactions in gaseous mixtures will not be treated in this section.

[1] Bredig and Walton, *Z. physik. Chem.*, **47**, 185 (1904).

Classification of Reactions

It is convenient to divide the study of these "slow" reactions into two divisions: (1) *Isolated reactions.* In these cases we have a single reaction to consider without the complication of any secondary reaction taking place at the same time. (2) *Simultaneous reactions.* In these cases we may have the products of the reaction recombining to give a back reaction, or we may have them reacting to produce new substances giving successive reactions, or we may have the reactants combining in more than one way to give side reactions.

It is also convenient to divide reactions into orders: (1) *Reactions of the first order, or unimolecular reactions,* in which a single molecule changes into one or more molecules. (2) *Reactions of the second order, or bimolecular reactions,* in which two molecules react to give one or more resulting molecules. Similarly, reactions of the third, fourth and up to the eighth order have been studied, but reactions of the higher orders are very rare. The great majority of chemical reactions are of the second or third orders.

Each order has a characteristic equation connecting the velocity of the reaction with the concentration of the reactants, so that, usually, we can easily tell from experimental data to which order a reaction belongs. The study of rate of reaction is based on the Law of Mass Action; suppose the following general equation represents a reaction taking place in a homogeneous system:

$$n_1A + n_2B + n_3C + \cdots = \text{any number of resultants.}$$

Then the rate of reaction $\propto [A]^{n_1}, [B]^{n_2}$, etc., where $[A], [B]$, etc., represent the concentration of A, B, etc. The rate of the complete reaction varies therefore as the product of these quantities, that is, $\propto [A]^{n_1} \times [B]^{n_2} \times [C]^{n_3} \cdots$. The application of this principle to the various classes of reactions will now be considered.

Isolated Reactions

First Order Reactions: The stoichiometric equations for these reactions would be of the form

$$A \rightarrow B;$$

or, more generally,

$$A \rightarrow B + C + D + \cdots.$$

Applying the principle of the mass action law we can state that the rate of change of the concentration of A at any instant is proportional to its concentration at that instant. It is evident therefore that the velocity of the reaction will vary continuously, starting with the highest value and tending finally to zero. Stating this mathematically we have:

$$-\frac{d(a-x)}{dt} \propto (a-x)$$

or

$$dx/dt \propto (a-x),$$

where a = number of moles of A originally present in 1 liter, and x = number of moles of A which changed to resultants in t minutes; $(a - x)$ represents the concentration of A after t minutes. Hence,

$$dx/dt = k_1(a - x),$$

where the constant k_1 is known as the velocity constant. It has a characteristic value for each reaction and is a measure of the rate of the reaction. By placing $x = 0$ and $a = 1$ we obtain the physical meaning of k_1, which may be described as the (calculated) number of moles of A disappearing per minute from one liter of solution containing one mole of A; the concentration of A is supposed to be kept constant at its initial value of one mole per liter. Integrating the expression

$$dx/dt = k_1(a - x)$$

and putting in the condition that, when $t = 0$, $x = 0$, we obtain

$$k = 1/t \ ln \frac{a}{a - x}.$$

Fig. 1 shows the curve obtained when the initial concentration of A is 0.1 mole per liter and when k has the value 0.23; all isolated reactions, independently of the order, have a curve of this form, in which the concentration of the reactants falls rapidly at first, gradually diminishing and tending finally to zero.

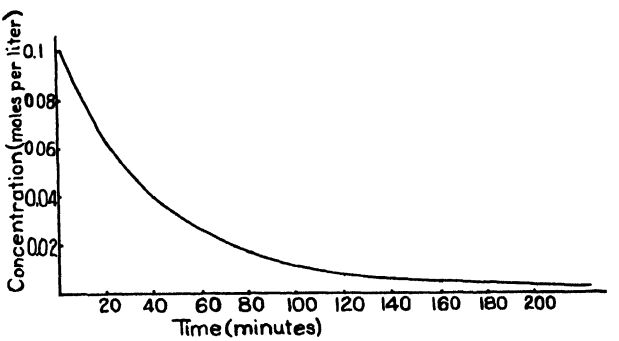


FIG. 1

The rate of the reaction at any point is given by the tangent at that point and inspection of the curve will show that the tangent has the highest value at the beginning of the reaction and falls proportionately to the concentration of A until when t becomes infinite, the value of the tangent is zero; obviously if we plot values of the concentration of A against corresponding values of the tangent, we obtain a straight line, because this line simply expresses the fact that the rate of change of A at any moment is proportiona' ɔ its concentration at that moment. A reaction which follows this equation would never reach completion but in practice the concentrations soon fall to negligible amounts;

in the example just quoted where the initial concentration is 0.1 mole per liter and k is 0.23, after 300 minutes the concentration of A falls to 0.1 per cent of its initial value.

A peculiarity of unimolecular reactions should be noted here, namely, that the concentration terms cancel out, and k would have the same value whether we considered one mole dissolved in one liter or in ten liters; therefore in the case of unimolecular reactions we may define k as the (calculated) number of moles of A disappearing per minute from a solution containing one mole of A.

Throughout this section the unit of time used will be the minute, and the unit of concentration moles per liter; on this basis k for most reactions that have been measured is a very small fraction.

If by some device the concentration, a, of the reacting substance be kept constant and equal to one mole per liter, the equation for the reaction velocity becomes

$$x = k \cdot at.$$

If the time for x to become equal to one mole be set equal to t', it follows that

$$t' = 1/k.$$

Under such circumstances, t' becomes an inverse measure of k. McBain [1] has suggested that the constant t' be used as the characteristic constant for the velocity of a chemical reaction.

Amongst the great number of measurements of velocity of chemical reactions there are none in which we are reasonably sure a unimolecular reaction is occurring; most of the examples given in the literature and in textbooks as unimolecular reactions are really pseudo-unimolecular reactions, which are treated in a later section.

Second Order Reactions: The stoichiometric equations for these reactions would be of the form

$$2A \rightarrow \text{one or more resultants,}$$

or generally

$$A + B \rightarrow \text{one or more resultants.}$$

Applying the principle of the mass action law in the first case, we can state that the rate of change of the concentration of A at any instant is proportional to the square of its concentration at that instant. Hence,

$$-d(a - x)/dt \propto (a - x)^2$$

or

$$dx/dt \propto (a - x)^2,$$

where a is the number of moles of A originally present in one liter and x is the number of moles of A which changed to resultants in t minutes; $(a - x)$ represents the concentration of A after t minutes. We have then

$$dx/dt = k_2(a - x)^2$$

[1] *Trans. Farad. Soc.*, **13**, 1 (1917); *Chem. News*, **116**, 315 (1917).

the integrated form of which is

$$k_2 = \frac{1}{t}\frac{x}{a(a-x)}.$$

This equation also applies when there are two reactants provided the initial concentrations are the same. Following the same reasoning in the second case we obtain: rate of the reaction after t minutes,

$$dx/dt \propto (a-x)(b-x),$$

where a and b are the number of moles per liter of A and B originally present, and x is the number of moles per liter of A or B which changed to resultants in t minutes; $(a-x)$ and $(b-x)$ therefore represent the concentrations of A and B respectively after t minutes. We have therefore

$$dx/dt = k(a-x)(b-x),$$

which on integration gives

$$k = \frac{1}{t(a-b)} ln \frac{b(a-x)}{a(b-x)}.$$

The velocity constant k is the (calculated) rate of disappearance of A or B in moles from a liter of solution containing one mole of A and one mole of B, the concentrations of A and B being supposed to be kept constant at their initial concentrations.

When the initial concentrations of A or B have values not far apart, a small error in either a or b becomes greatly magnified in the final result k; this may be avoided by using the equation in the following form:

$$k = \frac{1}{t}\left\{\frac{x}{ab} + \frac{a+b}{a^2b^2}\frac{x^2}{2} + \frac{a^2+ab+b^2}{a^3b^3}\frac{x^3}{3} + \cdots\right\},$$

obtained by expanding the logarithm and collecting the terms; for the early stages of the reaction, this series converges sufficiently rapidly to be used for calculating k, but usually it is better to have the initial concentration of one of the reactants at least twice that of the other, or have the concentrations equal and use the simple equation

$$k = \frac{1}{t}\cdot\frac{x}{a(a-x)}.$$

In these equations the velocity constant k is no longer independent of the unit of concentration employed for the reactants; using moles per liter and moles per cc. as our units of concentration, we shall obtain two velocity constants k_l and k_c respectively, where $k_l = k_c/1000$. It should be noted that when using the equation

$$k_2 = \frac{1}{t(a-b)} ln \frac{b(a-x)}{a(b-x)}$$

any convenient arbitrary unit of concentration may be used for calculating the term $\frac{b(a-x)}{a(b-x)}$ because its value is independent of the unit employed; the term $(a-b)$ should be calculated using moles per liter as the unit of concentration so that the velocity constant obtained is the (calculated) rate of disappearance of A or B in moles from a liter of solution containing one mole of A and one mole of B, the concentrations of A and B being supposed to be kept constant at their initial concentrations.

A number of bimolecular reactions have been studied among which is the action between sodium thiosulfate and alkyl halides [1] in dilute aqueous solution; the equation representing the change when methyl iodide is used is

$$CH_3I + S_2O_3^{--} = CH_3\ S_2O_3^{-} + I^{-},$$

so that the velocity is proportional to the concentration of the methyl iodide and to the concentration of the thiosulfate ion; the assumption is made that in dilute solution the sodium thiosulfate is almost completely ionized. The method of calculation will be illustrated by an example taken from Slator's work.

TABLE I

REACTION BETWEEN METHYL IODIDE AND SODIUM THIOSULFATE AT 25°, WITH AN EXCESS OF SODIUM THIOSULFATE

Time	0	4.75	10	20	35	55	∞
($Na_2S_2O_3$)	35.35	30.5	27.0	23.2	20.3	18.6	17.1
(CH_3I)	18.25	13.4	9.9	6.1	3.2	1.5	0
$\frac{b(a-x)}{a(b-x)}$	—	1.1751	1.4080	1.9635	3.2751	6.4017	
k	—	1.972	1.988	1.961	1.970	1.961	

The reaction was followed by withdrawing 10 cc. portions of the solution and titrating with 0.0101 N iodine, so that the concentrations of the reactants are first obtained in terms of the arbitrary unit "cc. of 0.0101 N iodine per 10 cc. of the reacting solution"; 35.35 therefore expresses the initial concentration a of the sodium thiosulfate in terms of this arbitrary unit and the figures that follow are values of $(a-x)$ in terms of the same unit: the final figure 17.1 represents the concentration of sodium thiosulfate when all the methyl iodide has reacted so that the initial concentration b of the methyl iodide is $35.35 - 17.1 = 18.25$ expressed in terms of the same arbitrary unit and values of $(b-x)$ are obtained by subtracting 17.1 from the values of $(a-x)$. From these data we can calculate values for $\frac{b(a-x)}{a(b-x)}$; the value of $(a-b)$ in terms of the arbitrary unit is 17.1, which, on conversion, gives $0.0101 \times 17.1 \div 10 = 0.0172$ mole per liter, so that we have all the necessary data for calculating the value of k from the formula

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)};$$

the average value of k is 1.97 which means that 1.97 moles of methyl iodide or sodium thiosulfate react per minute in one liter of an aqueous solution containing one mole of methyl iodide and one mole of sodium thiosulfate, the concentrations of these two reactants being

[1] Slator, *J. Chem. Soc.*, **85**, 1286 (1904).

supposed to be kept constant at their initial concentrations of one mole per liter; the solution from which this result was calculated contained initially 0.0357 *M* sodium thiosulfate and 0.0184 *M* methyl iodide. Slator showed that the same velocity constant was obtained when the methyl iodide was present in excess provided that the reaction occurred in dilute solution.

There are several special cases of bimolecular reactions which are usually found when one of the reactants is a catalyst; suppose we have a reaction between two substances A and B, the substance A being a catalyst; its concentration throughout the reaction will be unchanged so that we will have: rate of the reaction

$$dx/dt = k_2 a(b - x)$$

or

$$k_2 = \frac{1}{at} ln \frac{b}{b - x},$$

where a and b are the initial concentrations of A and B respectively, and x is the number of moles of B which react in t minutes. This equation also holds even if the substance A is not a catalyst provided its concentration is at least ten times that of B; in this case, we may consider the concentration of A to be constant because even at the very end of the reaction its concentration can only be reduced by 1/10. The hydration of acid anhydrides is an example of such a reaction, which may be represented in the case of acetic anhydride [1] by the following equation:

$$(CH_3CO)_2O + H_2O = 2CH_3COOH;$$

if the reaction is in moderately dilute solution, the concentration of the water will not vary appreciably. The isomeric change of nitrocamphor to the pseudo-form under the influence of hydroxyl ions [2] is another example, for the concentration of the catalyst remains constant throughout the reaction.

When a reaction is autocatalytic such as $A + B = 2A + C$ in which the substance B under the influence of the catalyst A breaks up into a substance C and the catalyst, we obtain

$$dx/dt = k_2(a + x)(b - x),$$

whence

$$k_2 = \frac{1}{t(a + b)} ln \frac{b(a + x)}{a(b - x)},$$

where a and b are the initial concentrations of A and B respectively and x is the amount of B which reacts in t minutes; $(a + x)$ and $(b - x)$ represent the concentrations of A and B after t minutes. This equation has been used in an investigation of the action between acetone and iodine [3] in aqueous solution.

Third Order Reactions: The stoichiometric equations for these reactions would be of the form

$$3A = R_1 + R_2 + \cdots$$

[1] Wilsdon and Sidgwick, *J. Chem. Soc*, **103**, 1959 (1913).
[2] Lowry and Magson, *J. Chem. Soc.*, **93**, 119 (1908).
[3] Rice and Kilpatrick, *J. Am. Chem. Soc.*, **45**, 1401 (1923).

or generally

$$A + B + C = R_1 + R_2 + \cdots.$$

Applying the principle of the mass action law as before, we have, in the first case,

$$-d(a - x)/dt \propto (a - x)^3$$

or

$$dx/dt \propto (a - x)^3,$$

where a is the number of moles of A originally present in one liter and x is the number of moles of A which changed to resultants in t minutes. $(a - x)$ represents the concentration of A after t minutes. We have then

$$dx/dt = k(a - x)^3$$

the integrated form of which is

$$k = \frac{1}{t} \cdot \frac{1}{2}\left\{ \frac{1}{(a - x)^2} - \frac{1}{a^2} \right\}.$$

Following the same reasoning in the second case, we obtain the rate of the reaction after t minutes,

$$dx/dt \propto (a - x)(b - x)(c - x),$$

where a, b and c are the number of moles respectively of A, B and C originally present per liter, and x is the number of moles per liter of A or B which changed to resultants in t minutes. $(a - x)$, $(b - x)$ and $(c - x)$ therefore represent respectively the concentrations of A, B and C after t minutes. We have then

$$dx/dt = k(a - x)(b - x)(c - x),$$

which on integration gives

$$k = \frac{1}{a'c't} ln \frac{a}{a - x} + \frac{1}{a'b't} ln \frac{b}{b - x} + \frac{1}{b'c't} ln \frac{c}{c - x},$$

where $a' = (a - b)$, $b' = (b - c)$, $c' = (c - a)$. The velocity constant k is the (calculated) rate of disappearance of A, B or C in moles from a liter of solution containing one mole of A, one mole of B and one mole of C, the concentrations of A, B and C being supposed to be kept constant at their initial concentrations; when calculating k, the terms $(a - b)$, $(b - c)$ and $(c - a)$ must be expressed in moles per liter, but the other concentration terms may be expressed in any convenient arbitrary unit. If the initial concentrations of A and B are equal or if the stoichiometric equation has the form $2A + C$ = one or more resultants, we have

$$dx/dt = k(a - x)^2(c - x),$$

whence

$$k = \frac{1}{t} \cdot \frac{1}{(c - a)^2}\left\{ \frac{(c - a)x}{a(a - x)} + ln \frac{c(a - x)}{a(c - x)} \right\}.$$

The reaction between ferric chloride and stannous chloride is claimed to be a trimolecular reaction,[1] since the equation which represents the change occurring in dilute aqueous solution can be written

$$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++};$$

as with other trimolecular reactions, secondary reactions take place and, when the conditions are varied, the constancy of k is not very satisfactory. As with bimolecular reactions, the velocity constant is dependent on the unit of concentration employed for the reactants; using moles per liter and moles per cc. as our units of concentration, we will obtain two velocity constants k_l and k_c respectively, but, in this case, $k_l = k_c/(1000)^2$. We can generalize this by stating that $k_l = k_c/(1000)^{n-1}$, where n is the order of the reaction.

Reactions of higher order than the third are very rare, and usually the velocity "constants" are far from satisfactory; the methods to be followed are exactly similar to those for reactions of lower orders.

When the initial concentration of one of the reactants A does not vary appreciably during the course of a reaction, the velocity equation becomes

$$dx/dt = ka(b - x)(c - x)$$

which on integration gives

$$k = \frac{1}{ta(b - c)(c - a)} ln \frac{c(b - x)}{b(c - x)};$$

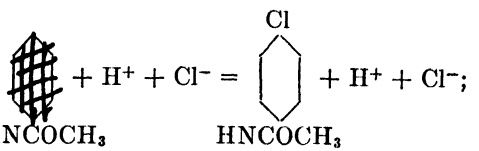
this occurs if A is a catalyst or if A is present in concentrations at least ten times as great as B or C. When the initial concentrations of two of the reactants A and B do not vary appreciably during the course of a reaction, the equation becomes

$$dx/dt = kab(c - x),$$

whence

$$k = \frac{1}{tab} ln \frac{c}{c - x};$$

this occurs if A and B are both catalysts or if their concentrations are relatively great compared with C. An example in which A and B are both catalysts is the conversion of acetyl-chloro-amino-benzene into parachloro-acetanilide[2] which is catalyzed by the simultaneous presence of hydrogen and chlorine ions as shown by the following equation:



[1] Noyes, *Z. physik. Chem.*, **16**, 546 (1895).
[2] Rivett, *Z. physik. Chem.*, **82**, 201 (1913).

in this case the concentrations of the hydrogen ion and of the chlorine ion, the a and b terms, are equal so that the equation becomes

$$k = \frac{1}{t \cdot a^2} ln \frac{c}{c - x} \cdot$$

Pseudo-unimolecular Reactions: Consider the reaction

$$A + B = C + \text{etc.};$$

if the substance B is a catalyst or if it is present in high concentration as compared with A, its concentration will not change appreciably throughout an experiment. In such cases, it has been found that the results of a single experiment give a constant value for k if substituted in the unimolecular equation

$$k = \frac{1}{t} ln \frac{b}{b - x} \cdot$$

Based on this fact, the custom has grown up of referring to such reactions as unimolecular; that one or more of the reactants happens to be present in constant concentration is a mere accidental circumstance and in no way affects the true order of the reaction: the classification of reactions should be based on the actual chemical equations which represent the change, so that attention is directed to essential similarities or differences rather than to non-essentials. The recent work of Kurt Meyer [1] has shown that the enolic form of aceto-acetic ester may be kept unchanged and even distilled, if quartz vessels are used so that no trace of alkaline catalyst is present; the equation for the isomeric change of aceto-acetic ester should therefore be written

$$CH_3COH : CHCOOC_2H_5 + OH^- = CH_3COCH_2COOC_2H_5 + OH^-$$

and the reaction is properly classed as bimolecular. The formation of para-chloro-acetanilide from acetyl-chloro-amino-benzene is catalyzed by the simultaneous presence of hydrogen and chlorine ions so that the reaction is probably trimolecular as shown by the equation already given in the preceding paragraph.

In the equation $A + B = C + D \cdots$, if the substance B is a catalyst, or if it is present in high concentration compared with A, we have

$$dx/dt \propto (a - x)b,$$

where a is the number of moles of A and B respectively originally present, and x is the number of moles of B which changed to resultants in t minutes. $(a - x)$ and b therefore represent the concentrations of A and B respectively after t minutes. We have, therefore,

$$dx/dt = k_2 b(a - x),$$

which on integration gives

$$k_2 = \frac{1}{tb} ln \frac{a}{a - x};$$

[1] *Ber.*, **53**, 1410 (1920).

if we are dealing with such a change and we substitute the results in the unimolecular equation

$$k_1 = \frac{1}{t} ln \frac{a}{a - x},$$

we will obtain a constant; this constant ($k_2 b$) is not of course characteristic of the reaction, for, without a knowledge of the concentration of the substance B, the measurement would be valueless. The true bimolecular constant for the reaction may be obtained in such a case by dividing the "pseudo-unimolecular" constant ($k_2 b$) by b, the concentration of the substance B.

If the substance B is in high concentration compared to A, the equation

$$k = \frac{1}{t(a - b)} ln \frac{b(a - x)}{a(b - x)}$$

readily reduces to

$$k = \frac{1}{tb} ln \frac{a}{a - x}$$

because we can write (approximately) $b - x = b$ and $a - b = -b$. In the same way the equation for a trimolecular reaction reduces to

$$k = \frac{1}{tab} ln \frac{c}{c - x}$$

when the reactants A and B are present in relatively high concentration compared to the reactant C; by using these equations we obtain a constant which is truly characteristic of the reaction rather than a "constant" which depends on the concentration of one or more of the reactants.

Summary: In all the equations given below $a, b, c, \cdots$ represent the initial concentrations in moles per liter of the reactants $A, B, C, \cdots$, and x represents the number of moles of A which react in t minutes.

(1) For unimolecular reactions, $A = B + C + \cdots$, we have:

$$\frac{d(a - x)}{dt} = k_1(a - x); \qquad k_1 = \frac{1}{t} ln \frac{a}{a - x}.$$

(2) For bimolecular reactions, $A + B = C + D + \cdots$, we have:

$$dx/dt = k_2(a - x)(b - x); \qquad k_2 = \frac{1}{t(a - b)} ln \frac{b(a - x)}{a(b - x)}.$$

The following special cases may occur:

(a) When the initial concentrations of A and B are equal or when the stoichiometric equation has the form $2A = C + D + \cdots$, we have:

$$dx/dt = k_2(a - x); \qquad k_2 = \frac{1}{t} \frac{x}{a(a - x)}.$$

(*b*) When the substance A is a catalyst or when its concentration is more than ten times that of B, we have:

$$dx/dt = k_2(a - x)b; \qquad k_2 = \frac{1}{tb} ln \frac{a}{a - x}.$$

(*c*) When the reaction is autocatalytic, $A + B = C + 2A$, we have:

$$dx/dt = k_2(a + x)(b - x); \qquad k_2 = \frac{1}{t(a + b)} ln \frac{b(a + x)}{a(b - x)}.$$

(3) For trimolecular reactions, $A + B + C = D + \cdots$, we have:

$$dx/dt = k_3(a - x)(b - x)(c - x);$$

$$k_3 = \frac{1}{a'c't} ln \frac{a}{a - x} + \frac{1}{a'b't} ln \frac{b}{b - x} + \frac{1}{b'c't} ln \frac{c}{c - x},$$

where $a' = (a - b)$, $b' = (b - c)$ and $c' = (c - a)$.

The following special cases may occur:

(*a*) When the reactants have all the same initial concentration or when the stoichiometric equation has the form $3A = D + \cdots$, we have:

$$dx/dt = k_3(a - x)^3; \qquad k_3 = \frac{1}{t} \cdot \frac{1}{2} \left\{ \frac{1}{(a - x)^2} - \frac{1}{a^2} \right\}.$$

(*b*) When two of the reactants have the same initial concentration or when the stoichiometric equation has the form $2A + C = D + E + \cdots$, we have:

$$dx/dt = k_3(a - x)^2(c - x); \qquad k_3 = \frac{x}{at(a - x)(c - a)} + \frac{1}{t(c - a)^2} ln \frac{c(a - x)}{a(c - x)}.$$

(*c*) When the substance A is a catalyst or when its concentration is more than ten times that of B or C, we have:

$$dx/dt = k_3a(b - x)(c - x); \qquad k_3 = \frac{1}{ta}(b - c)(c - a) ln \frac{c(b - x)}{b(c - x)}.$$

(*d*) When A and B are both catalysts or when their initial concentrations are more than ten times that of C, we have:

$$dx/dt = k_3ab(c - x); \qquad k_3 = \frac{1}{tab} ln \frac{c}{c - x}.$$

(4) For quadrimolecular reactions, $A + B + C + D = \cdots$, we have:

$$dx/dt = k_4(a - x)(b - x)(c - x)(d - x).$$

In the special case in which the initial concentrations of all the reactants are the same, this becomes:

$$dx/dt = k_4(a - x)^4; \qquad k_4 = \frac{1}{t} \cdot \frac{1}{3} \left\{ \frac{1}{(a - x)^3} - \frac{1}{a^3} \right\}.$$

Simultaneous Reactions

Opposing Reactions: The simplest example of such a reaction would be represented by $A \rightleftarrows B$, where we have two simultaneous reactions occurring in the reacting system, the direct change $A \rightarrow B$ and the opposed reaction $B \rightarrow A$; the net velocity of the reaction at any moment will be given by the difference of these two velocities. The concentration of A, and hence the velocity of the direct reaction, is greatest at the commencement of the change, and both diminish as the reaction proceeds; the concentration of B, and hence the velocity of the reverse reaction, is least at the commencement of the change, but both increase as the reaction proceeds; it is evident therefore that finally the rates of the two opposed reactions will become equal and we shall have a state of equilibrium. It may be noted that our classification of isolated reactions is really artificial for no reactions go to completion: our "isolated" reactions finally reach a state of equilibrium, but the equilibrium point is very near to one side because the velocity of the reverse change is negligibly small.

The principle we apply in the treatment of such simultaneous changes is that we can apply the Law of Mass Action to each reaction independently of any other reactions occurring at the same time; thus, in the above reaction $A \rightleftarrows B$, the rate of change of A at any instant is proportional to the concentration of A at that instant; this statement is not affected by the fact that the rate of change of B into A at any instant is proportional to the concentration of B at that instant. We have then: the velocity of the direct reaction, $A \rightarrow B$, after t minutes is proportional to $(a - x)$ or equal to $k_1(a - x)$; the velocity of the reverse reaction, $B \rightarrow A$, after t minutes is proportional to $(b + x)$ or equal to $k_2(b + x)$; therefore, the velocity of the total change after t minutes is given by the equation

$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_1(a - x) - k_2(b + x) = (k_1 a - k_2 b) - (k_1 + k_2)x,$$

where a and b are the number of moles respectively of A and B originally present in one liter, and x is the number of moles of A which changed to B in t minutes. $(a - x)$ and $(b + x)$ represent the respective concentrations of A and B after t minutes. Integrating, we find that

$$k_1 + k_2 = \frac{1}{t} ln \frac{A}{A - x},$$

where

$$A = (k_1 a - k_2 b)/(k_1 + k_2).$$

Consider the reaction at the equilibrium point when the velocities of the two opposed changes are equal; we can then write

$$k_1(a - x_e) = k_2(b + x_e),$$

where the subscript ϵ signifies equilibrium concentrations. Then

$$\frac{(b + x_\epsilon)}{(a - x_\epsilon)} = \frac{k_1}{k_2} = K,$$

where K is the equilibrium constant of the reaction. We cannot apply these equations because, at present, we have no examples of unimolecular chemical reactions which proceed with measurable speed; the examples of opposing unimolecular reactions usually quoted are bimolecular or trimolecular reactions.

The simplest examples of opposing bimolecular reactions are to be found in isomeric changes which take place under the influence of acid or alkali. The stoichiometric equation for such a change in alkaline solution is: $A + OH^- = B + OH^-$. By following the same method as before we find that the velocity of the total change at time t is,

$$dx/dt = k_1(a - x)c - k_2(b + x)c = c(k_1a - k_2b) - c(k_1 - k_2)x,$$

where a, b and c are the number of moles respectively of A, B and hydroxyl ion originally present in one liter, and x is the number of moles of A which changes to B in t minutes; $(a - x)$ and $(b + x)$ represent the respective concentrations of A and B after t minutes; the concentration of the catalyst is unchanged. Integrating, we find that

$$\frac{1}{ct} ln \frac{A}{A - x} = k_1 + k_2,$$

where

$$A = \frac{k_1a - k_2b}{k_1 + k_2}.$$

If we consider the reaction at the equilibrium point, we have, as before:

$$k_1(a - x_\epsilon)c = k_2(b + x_\epsilon)c,$$

so that

$$\frac{b + x_\epsilon}{a - x_\epsilon} = \frac{k_1}{k_2} = K,$$

where K is the equilibrium constant of the reaction. The concentration of the catalyst disappears from the equation in accordance with the well-known rule that, in dilute solution, where the mass action law applies, the catalyst does not affect the equilibrium point. These equations have been used in several investigations [1] and, in a semi-quantitative kind of way, the mass action law has been shown to hold; it seems desirable, however, to investigate a simple case of isomerism more fully and accurately than has been done. It may be, however, that even in isomeric changes the simple stoichiometric equations do not represent the reactions which occur in the solution; this is almost

[1] Küster, *Z. physik. Chem.*, **18**, 171 (1895); Koelichen, *ibid.*, **33**, 129 (1900); Trey, *ibid.*, **18**, 198 (1895); Lowry, *J. Chem. Soc.*, **75**, 227 (1899).

certainly the case in the acid hydrolysis of esters; using methyl acetate, the stoichiometric equation is

$$CH_3COOCH_3 + H_2O \rightleftarrows CH_3COOH + CH_3OH,$$

whereas the actual reaction taking place in the solution consists of at least two reactions which may perhaps be represented by some such scheme as the following:

$$CH_3COOCH_3 + H_2O \rightleftarrows CH_3COOCH_3.H_2O,$$
$$CH_3COOCH_3.H_2O + H^+ \rightleftarrows CH_3COOH + CH_3OH + H^+.$$

We have therefore at least two successive states of equilibrium instead of the simple equilibrium postulated in the stoichiometric equation; a more detailed discussion of this will be given later. It is probable that any such discussion of opposing reactions in solution is quite inadequate if it does not include some consideration of the combinations between the reactants and the solvent which probably occur in all solutions.

Consecutive Reactions: The treatment of consecutive reactions is very complicated and has been successful only in a few special cases; these will be used to illustrate the method of treating consecutive reactions. The hydrolysis of ester by alkali probably consists of two reactions, which may be written for ethyl acetate and sodium hydroxide as follows:

$$CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOC_2H_5.H_2O, \quad (1)$$

$$CH_3COOC_2H_5.H_2O + OH^- \rightleftarrows CH_3COO^- + C_2H_5OH + H_2O. \quad (2)$$

We have therefore two consecutive bimolecular reactions. Hydration reactions usually occur practically instantaneously so that as the hydrolysis proceeds reaction (1) will be continually adjusting itself to the changing conditions, and at all periods of the reaction we can assume that the ethyl acetate hydrate will be present at the equilibrium concentration; since the affinity of ethyl acetate for water is probably small, the equilibrium concentration of the hydrate will be small, so that, at any moment, the concentration of ethyl acetate hydrate will be proportional to the concentration of the unhydrated form and therefore to the total ethyl acetate in the solution, since, in dilute solution, the concentration of the water will be constant. A study of the kinetics of the reaction in dilute solution would show that the velocity of the reaction was proportional to the concentration of the ethyl acetate and to the concentration of the sodium hydroxide, so that we would be tempted to write the equation for the change that occurs in the solution as

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH;$$

however, when we measure the velocity in stronger solutions or in the presence of neutral salts, this simple equation fails and it becomes necessary to adopt some such scheme as shown by equations (1) and (2).

In such reactions as the hydrolysis of ethyl acetate which consist of a very fast reaction followed by a slow reaction, the kinetic equation may not indicate the existence of the fast reaction at all; this is usually the case in any series of reactions occurring consecutively, which consist of one slow reaction, the others being comparatively very fast; the speed of the complete reaction and its order are fixed by the slow reaction, and the fast reactions usually escape notice altogether, at any rate in dilute solution. It is evident that this often occurs when the actual reactants are not those represented in the stoichiometric equation, but compounds with the solvent; for, if the equilibrium conditions are such that the concentrations of these solvated molecules (the true reactants) are proportional to the concentrations of the stoichiometric reactants, the stoichiometric equation will appear to represent the change completely. In strong solution, or when we alter the solvent, the simple kinetic equation developed for dilute solutions usually fails; this result indicates the presence of other reactions. It is important, therefore, to study reactions under different conditions so that the true character of the reaction may be determined and that it may be properly classified.

Sometimes, even in dilute solution there is an obvious abnormality which can be explained by the presence of a series of reactions containing only one slow reaction; the reaction between bromine and acetone in aqueous solution which was first studied by Lapworth [1] is such an example; as might be expected from the stoichiometric equation

$$CH_3COCH_3 + Br_2 + H^+ \rightleftarrows CH_3COCH_2Br + Br^- + 2H^+,$$

the velocity is proportional to the concentration of the acetone and to the concentration of the hydrogen ions, but the velocity is quite independent of the concentration of the bromine. Lapworth explained this by saying that the change consists of a series of reactions, the first being the slow change whose velocity is measured, followed by two rapid changes, represented as follows:

$$CH_3COCH_3 + H^+ \rightleftarrows CH_3COH : CH_2,$$
$$CH_3COH : CH_2 + Br_2 = CH_2C(OH)BrCH_2Br,$$
$$CH_3C(OH)BrCH_2Br = CH_3COCH_2Br + HBr.$$

He supposes that acetone in aqueous solution exists in two forms, keto and enol in equilibrium; the enolic form reacts instantaneously with bromine and the resulting compound instantaneously splits out hydrobromic acid, but the ketonic form does not react with bromine: evidently the action of the hydrogen ions is to convert slowly the ketonic form of acetone into the enolic form and this is the reaction whose kinetics we are studying, since the velocity of this reaction would be proportional to the concentrations of the acetone and the hydrogen ion, but would be independent of the concentration of the bromine.

The hydrolysis of an ester of a dibasic acid by alkali is a more complicated example of consecutive reactions; the following equations probably represent

[1] *J. Chem. Soc.*, **85**, 30 (1904).

the successive reactions for the hydrolysis of ethyl oxalate:

$$(COOC_2H_5)_2 + 2H_2O \rightleftarrows \begin{matrix} COOC_2H_5.H_2O \\ | \\ COOC_2H_5.H_2O \end{matrix} \quad \text{Very fast,} \qquad (1)$$

$$\begin{matrix} COOC_2H_5.H_2O \\ | \\ COOC_2H_5.H_2O \end{matrix} + OH^- = \begin{matrix} COOC_2H_5.H_2O \\ | \\ COO^- \end{matrix} + C_2H_5OH + H_2O \quad \text{Slow,} \qquad (2)$$

$$\begin{matrix} COOC_2H_5.H_2O \\ | \\ COO^- \end{matrix} + OH^- = \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + C_2H_5OH + H_2O \quad \text{Slowest.} \qquad (3)$$

Many such investigations have been made[1]; in general the velocity of reaction (2) is much greater than reaction (3); for ethyl oxalate, ethyl malonate and methyl succinate the respective ratios are 20,000, 70 and 5. Similar results have been obtained for the hydrolysis of esters of tribasic acids such as triacetin.[2] Many other studies of consecutive reactions have been made but in most cases there is a great deal of uncertainty as to the mechanism of the reactions occurring in the solution; the whole subject of consecutive reactions is in a very unsatisfactory condition and it is desirable to have a few simple cases investigated in which we are fairly certain of the mechanism of the reactions occurring.

Side Reactions: The transformation of a substance is often accomplished by a number of independent reactions which furnish different end products, and which are known as side reactions: usually one of the reactions predominates and is called the main or principal reaction, the others being called secondary reactions. The conditions of the experiment determine the relative rates of the side reactions; by altering those we can alter the relative rates, sometimes to such an extent that a secondary reaction becomes the main or principal reaction. The example commonly given of side reactions is the decomposition in aqueous solution of hydroxylamine, which is represented as follows:

$$3NH_2OH = NH_3 + N_2 + 3H_2O,$$
$$4NH_2OH = 2NH_3 + N_2O + 3H_2O.$$

In studying these reactions, we apply the same principle that we used for other simultaneous reactions, namely, that each reaction proceeds independently of the others and the mass action law may be applied to each just as if the others were not present; for example, in a solution of cane sugar and ethyl acetate containing hydrochloric acid, the hydrolysis of the ester and the inversion of

[1] Skrabal and Singer, *Monatsh.*, **41**, 339 (1920), **40**, 363 (1919); Pinnow, *Z. Elektrochem.*, **24**, 21 (1918); Yamazaki, *J. Tokio. Chem. Soc.*, **40**, 198 (1919).

[2] Geitel, *J. prakt. Chem.*, **55**, 429 (1897); Meyer, *Z. Elektrochem.*, **13**, 485 (1907); Abel, *Z. physik. Chem.*, **56**, 558 (1906).

the sugar proceed independently. The method of study of these changes may be illustrated by reference to the following simple change:

$$A \rightarrow B, \tag{1}$$

$$A \rightarrow C. \tag{2}$$

The rate of the reaction $A \rightarrow B$ after t minutes is proportional to $(a - x)$ or equal to $k_1(a - x)$; the rate of the reaction $A \rightarrow C$ after t minutes is proportional to $(a - x)$ or equal to $k_2(a - x)$, where a is the number of moles of A per liter originally present, and x is the number of moles per liter of A which changed (to B and C) in t minutes; $(a - x)$ is therefore the concentration of A after t minutes. Since the rate of decomposition of A, dx/dt, must equal the sum of the rates of formation of B and C, we have

$$dx/dt = k_1(a - x) + k_2(a - x) = (a - x)(k_1 + k_2).$$

Integrating,

$$k_1 + k_2 = \frac{1}{t} ln \frac{a}{a - x}.$$

To evaluate k_1 and k_2 we must know some other relation between them, which may be obtained in the following manner:

$$\frac{\text{The rate of formation of } B \text{ after } t \text{ minutes}}{\text{The rate of formation of } C \text{ after } t \text{ minutes}} = \frac{k_1(a - x)}{k_2(a - x)} = \frac{k_1}{k_2} = \text{a constant.}$$

If this ratio of the rates is a constant at all stages of the reaction, we must have:

$$\text{The rate of formation of } B \text{ after } t \text{ minutes}$$
$$\text{The rate of formation of } C \text{ after } t \text{ minutes}$$
$$= \frac{\text{Total amount of } B \text{ present after } t \text{ minutes}}{\text{Total amount of } C \text{ present after } t \text{ minutes}}.$$

The most convenient time to estimate the relative amounts of B and C formed, and thus determine k_1/k_2, is at the end of the experiment; since we know $k_1 + k_2$ we can determine each. The principle "that the ratio of the amounts of substances formed in the side reactions is independent of the time" is characteristic of side reactions and is a means of distinguishing them from opposing or consecutive reactions.[1] It should be noted, however, that this holds only when the side reactions in any experiment are all of the same order; if this is not the case, it can easily be shown that the ratio of the amounts of the products is not independent of the time. Reactions of benzene derivatives provide ample opportunities for the study of side reactions and several such investigations have been made.[2]

[1] Wegscheider, *Z. physik. Chem.*, **30**, 593 (1899).

[2] Holleman, *Z. physik. Chem.*, **31**, 79 (1899); Wegscheider, *Z. physik. Chem.*, **34**, 290 (1900); Slator, *J. Chem. Soc.*, **83**, 729 (1903).

Order and Mechanism of a Reaction: When discussing the mechanism of a chemical reaction it is important to distinguish carefully between the stoichiometric equation of the change and the equation which truly represents the reaction taking place in the solution. If we have calcium hydroxide and methyl acetate in dilute aqueous solution, the stoichiometric equation of the change would be

$$2CH_3COOCH_3 + Ca(OH)_2 = (CH_3COO)_2Ca + 2CH_3OH,$$

whereas the equations representing the actual change are probably:

$$CH_3COOCH_3 + H_2O \rightleftarrows CH_3COOCH_3.H_2O,$$
$$CH_3COOCH_3\ H_2O + OH^- = CH_3COO^- + CH_3OH.$$

The measurement of rate of reaction is a valuable method for finding the mechanism of the actual changes which occur in the solution. The simplest method of applying the results of a measurement of rate of reaction is to substitute corresponding values of concentration of reactants and time in the velocity equation for the various orders; a number of sets of values of k will then be obtained corresponding to the different velocity equations, which are sufficiently different so that not more than one velocity equation will give a constant series of values for k; we can therefore identify the order of the reaction. When using this method it is important to do several experiments using different initial concentrations of the reactants; for example, in the hydrolysis of methyl acetate in a dilute aqueous solution of hydrochloric acid, if we substitute corresponding values of the concentration of the methyl acetate in an aqueous solution of hydrochloric acid, a unimolecular constant is obtained: if, however, we repeat the experiment using a different concentration of hydrochloric acid, we shall obtain a constant, but it will be different from that obtained previously, indicating that the reaction is not unimolecular. If, however, we substitute the results in the bimolecular equation

$$k_2 = \frac{1}{tb} ln \frac{a}{a - x},$$

where the a and b terms refer to concentrations of ester and acid respectively, we shall obtain a constant since the concentration of hydrogen ion b remains practically constant during the experiment. So long as the reaction is carried out in dilute aqueous solution this equation will give a constant value for k which would indicate that the reaction is bimolecular. If however we do the reaction in stronger solutions of the ester, the velocity constant begins to drift and increases as the concentration of the ester increases; finally, it becomes evident that, to explain the results, we have to assume that the hydrolysis of the ester by hydrochloric acid occurs by consecutive reactions in some such manner as the following:

$$CH_3COOCH_3 + H_2O \rightleftarrows CH_3COOCH_3.H_2O \qquad \text{Rapid,}$$
$$CH_3COOCH_3.H_2O + H^+ \rightleftarrows CH_3COOH + CH_3OH \quad \text{Slow.}$$

If the methyl acetate is not hydrated to a great extent, the concentration of the ester hydrate will be proportional to the total concentration of the ester in dilute aqueous solution; hence, in dilute aqueous solution, the rate of hydrolysis will be proportional to the stoichiometric concentration of ester and to the concentration of hydrogen ion. In stronger solutions of the ester the proportionality between the total ester and the hydrate no longer holds; the dissociation of the acid is also affected so that the conditions are very complicated and will be discussed more fully later.

It is evident, therefore, that when studying the order and the mechanism of a chemical reaction by making measurements of the rate, it is not sufficient to make measurements under the same conditions; such measurements would be very likely to lead to erroneous conclusions; only by varying the concentrations of the different reactants over wide ranges and comparing the corresponding velocity constants, can we determine confidently the order and mechanism of a reaction. Usually, we find these much more complicated than we would suspect from the stoichiometric equations.

When there are simultaneous reactions, especially opposed reactions or consecutive reactions, the method just described is usually not suitable for investigating the mechanism of a reaction; in such cases it is necessary to confine the measurements to the early stages of the reaction, because the opposed or consecutive reactions are comparatively unimportant during the early stages; since only small quantities of the reacting substances disappear during the period of measurement, the precision of k will not be very high unless great care is taken with the analytical procedure. Instead of measuring k in the early stages of the reaction we may measure the time required for a certain fraction of the reactants to become transformed to resultants, and by doing several experiments using different concentrations of reactants we can find the relation between the time and the initial concentration; in the general form, this relation is

$$t \propto \frac{1}{a^{n-1}},$$

where n is the order of the reaction, t is the time required for transformation of a certain fraction of the reactants and a is the initial concentration. The time taken to transform say 1/5 of the reactant in a unimolecular reaction is obtained by substituting $x = a/5$ in the unimolecular equation

$$t = \frac{1}{k} ln \frac{a}{a - x},$$

whence

$$t_{1/5} = \frac{1}{k} ln \frac{5}{4},$$

so that the time of 1/5 change is independent of the initial concentration of the

reactant; substituting similarly in the bimolecular equation

$$t = \frac{x}{at(a - x)},$$

we obtain

$$t_{1/5} = \frac{\text{Constant}}{a},$$

so that for bimolecular reactions the time of 1/5 change is inversely proportional to the initial concentration of the reactants.

Another useful method for investigating the mechanism of a reaction is to measure the velocity under conditions such that the concentration of only one of the reactants A is changing; by having the initial concentration of A from 1/10 to 1/1000 of the initial concentration of any of the other reactants we may assume that the concentrations of these remain approximately constant throughout the experiment; in this way we obtain a simplification of the equation for the reaction and when we find the equation which gives a constant for k we also determine the number of molecules of A taking part in the reaction. The experiment is then repeated having A present in high concentration and another reactant B present in low concentration; the velocity equation which gives constant values for k now determines the number of molecules of B taking part in the reaction; and similarly for the other reactants. This method is limited unless we can measure the rate of the reaction by measuring the rate of appearance of one of the resultants; if we measured the rate of the reaction by the rate of disappearance of the reactants, we would have to develop an analytical method for each reactant in turn and this would only rarely be possible.

Reaction Velocity and Temperature: The velocities of chemical reactions, almost without exception, increase rapidly with rise of temperature; the reaction between acetone and iodine proceeds seventy-five times as fast at 35° as it does at 0° and this behavior is characteristic of all reactions whose velocities can be measured. It has been found that a straight line is obtained by plotting values of the logarithm of the velocity constant of a reaction against $1/T$, where T is the absolute temperature, so that the equation representing the variation of the velocity constant with temperature would have the form

$$\log k = C - a/T,$$

where C and a are constants. When the range of temperature is large or the data are very accurate, the locus will differ slightly but progressively from a straight line, so that we must add correction terms in the usual manner, obtaining

$$\log k = C - a/T - bT - cT^2 - \cdots.$$

The number of terms to be taken will depend on the range of temperature and the precision of the data. Differentiating the simple equation

$$\log k = C - a/T,$$

we obtain

$$d \log k/dt = a/T^2;$$

this equation was used by Arrhenius and will be written in the form

$$\frac{dlnk}{dT} = \frac{Q}{R} \cdot \frac{1}{T^2},$$

where Q is a constant and R is the gas constant. Integrating this equation between the limits k_1, T_1 and k_2, T_2, we obtain

$$ln\frac{k_1}{k_2} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

which represents in a fairly satisfactory manner the effect of temperature on velocity of reaction. The Arrhenius equation may be written

$$1/k \cdot dk/dT = A/T^2,$$

where $1/k \cdot dk/dT$ is the temperature coefficient of a reaction, i.e., the increase of the velocity per unit velocity per degree rise in temperature; the rate of increase with temperature of rate of reaction will therefore diminish with rise in temperature. The custom among chemists is to call the ratio of the velocities at two temperatures 10° apart the temperature coefficient; usually 35° and 25° are selected so that k_{35}/k_{25} is usually referred to as the temperature coefficient of a reaction. For the range 35° to 25°, the Arrhenius equation becomes

$$2.3026 \log\frac{k_1}{k_2} = \frac{Q}{1.9864}\left(\frac{1}{298.1} - \frac{1}{308.1}\right),$$

so that

$$\log\frac{k_1}{k_2} = \frac{Q}{42{,}011}.$$

For the hydrolysis of cane sugar by hydrochloric acid the value of Q is 26,000 and k_{35}/k_{25} is 4.13; for the hydrolysis of methyl acetate by sodium hydroxide, Q is 10,900 and k_{35}/k_{25} is 1.82; these two examples represent the limits of the variation and it is only very rarely that a reaction has a temperature coefficient greater than that obtaining in the hydrolysis of cane sugar or less than that in the corresponding reaction with methyl acetate.

Reaction Velocity and Pressure: In the last century several studies[1] were made which showed that pressure caused appreciable alteration in velocity of reaction. Rothmund confirmed the earlier work of Röntgen and showed that the velocity of hydrolysis of cane sugar decreases about 1 per cent per 100 atmospheres; he also showed that the hydrolysis of methyl and ethyl acetates by hydrochloric acid increased with pressure, the increase being about 3.7

[1] Röntgen, *Ann. Phys. Chem.*, **45**, 98 (1892); Rothmund, *Z. physik. Chem.*, **20**, 168 (1896); Stern, *Ann. Phys. Chem.*, **59**, 652 (1896); Bogojawlensky and Tammann, *Z. physik. Chem.*, **23**, 13 (1897).

per cent per 100 atmospheres. Stern and also Bogojawlensky and Tammann found that pressure increased the catalytic activity of weak acids much more than strong acids; when weak acids are used as catalysts the rate of hydrolysis of cane sugar is increased by pressure, and the pressure coefficient of the velocity hydrolysis of methyl acetate is greater for weak acids than for strong acids. Cohn and de Boer [1] made a comprehensive study of the influence of pressure on the rate of hydrolysis of cane sugar and they give a critical review of the older work; they show that the reaction velocity is decreased 8 per cent at 500 atmospheres, 19 per cent at 1000 atmospheres and 26 per cent at 1500 atmospheres. The work was continued by Cohen and Valeton,[2] using acetic acid as catalyst; as shown by Stern, the velocity increases with pressure, but the pressure coefficient diminishes with increase of pressure until, above 1000 atmospheres, the velocity is almost independent of the pressure. Cohen and Kaiser [3] studied the effect of pressure on the hydrolysis of ethyl acetate by sodium hydroxide and obtained the following results, shown in Table II. Moesveld [4] has studied the pressure coefficient of the

TABLE II

EFFECT OF PRESSURE ON THE HYDROLYSIS OF ETHYL ACETATE BY SODIUM HYDROXIDE. TEMPERATURE 2.40°

p (atmospheres)	1	250	500	750	1000	1250	1500
k (per cent increase)	.—	3.7	11.9	18.5	25.5	30.9	37.4

velocity of reaction of the change

$$5HBr + HBrO_3 = 3Br_2 + 2H_2O.$$

He shows that it is negative and independent of the temperature; the velocity of the reaction at 1500 atmospheres is 15.4 per cent less than at 1 atmosphere.

MEASUREMENT OF RATE OF REACTION

The Velocity Constant: When measuring rate of reaction the reactants are usually present at arbitrary concentrations; in order to have measurements comparable, it is necessary to calculate the velocity at some standard concentration of the reactants by means of the velocity equations already given. Suppose we have a reaction $A + B + HCl$, where A and B are two substances which react under the influence of the hydrochloric acid, the whole reaction being in dilute aqueous solution; usually, this equation will not represent the reaction which takes place in the solution because the hydrochloric acid will dissociate and the substances A and B will often form hydrates or combine with each other, so that the actual reaction which takes place in the solution is

[1] *Z. physik. Chem.*, **84**, 41 (1913).
[2] *Z. physik. Chem.*, **92**, 433 (1917).
[3] *Z. physik. Chem.*, **89**, 338 (1915).
[4] *Z. physik. Chem.*, **103**, 486 (1923).

quite different from that represented by the stoichiometric equation of the change. It would be most desirable to write down the equation which represents the change actually occurring in the solution and then calculate the velocity per unit concentration of the actual reactants; unfortunately this is not possible as yet because of our lack of knowledge of homogeneous solution; the hydrochloric acid is present as undissociated molecule, hydrated hydrogen ion and unhydrated hydrogen ion and as chloride ion, hydrated and unhydrated; there is no general agreement as to whether only one of these is catalytically active or whether all of them are active; even if we knew which were active there is no reliable method of measuring the concentration for strong acids like hydrochloric acid; further, we have no method of measuring the concentrations of the hydrated forms of A or B should the reaction include them. In these circumstances it is best to give the velocity constant per unit concentration of the materials added to the solution; thus, the value of k for the above reaction would be the (calculated) number of moles of A or B disappearing per minute from 1 liter of a solution containing 1 mole of A, 1 mole of B and 1 g. equivalent of hydrochloric acid. The complete statement of the velocity constant should give the value of k calculated in the above manner and also the actual concentrations of A and B and the hydrochloric acid used in the experiment: with these data available, it will be an easy matter to recalculate k at any time when our knowledge of solution problems is more advanced.

Errors of Measurement: When measuring velocity of reaction the precision measure of the result should always be stated because, although the velocity of a given reaction may be varied widely by altering the conditions, the temperature coefficient is usually only slightly affected, and, from theoretical considerations, a knowledge of the temperature coefficient and its variation is even more important than a knowledge of the velocity. The reaction between acetone and iodine will be used as an illustration in the following discussion of the errors which may arise in measuring rate of reaction.

In dilute aqueous solution, acetone and iodine react extremely slowly but acids catalyze the reaction, and the velocity is proportional to the concentration of the acetone and the acid but is independent of the concentration of the iodine. Therefore, if the solution contains initially b moles of acetone and a moles of acid per liter, and after t minutes x moles of acetone have reacted with iodine, the concentration of the acetone is then $(b - x)$ moles per liter, and that of the acid is $(a + x)$ moles per liter. Therefore,

$$dx/dt = k(a + x)(b - x),$$

which on integration gives

$$k = \frac{1}{t(a + b)} ln \frac{b(a + x)}{a(b - x)},$$

where the velocity constant k is the (calculated) rate of disappearance of acetone in moles from a liter of solution containing 1 mole of acetone, 1 g. equivalent of hydrochloric acid and about 0.01 g. equivalents of iodine, since the rate of the reaction is independent of the concentration of the iodine, its exact concentration need not be stated. The measured quantities from which we calculate k are t, a, b and x. To find the error in k caused by a deviation

in one of the directly measured quantities we must take the partial differential of k with respect to the quantity and multiply by its deviation.

$$\frac{\partial k}{\partial t} = -\frac{1}{(a+b)}\left[\log\frac{b(a+x)}{a(b-x)}\right]\frac{1}{t^2} = -\frac{k}{t},$$

$$\frac{\partial k}{\partial a} = -\frac{k}{(a+b)}\left[1+\frac{x}{akt(a+x)}\right] = -\frac{k}{a}\text{ (approximately)},$$

$$\frac{\partial k}{\partial b} = -\frac{k}{(a+b)}\left[1+\frac{x}{bkt(b-x)}\right] = -\frac{k}{b}\text{ (approximately)},$$

$$\frac{\partial k}{\partial x} = \frac{1}{t(a+x)(b-x)}.$$

These approximations hold if, in the experiments, a approximates b, and $x/a^2kt = 1$ approximately. Hence the deviation in k caused by a deviation δ_t in t is

$$_k\Delta_t = \frac{k}{t}\delta_t.$$

Similarly, for the other quantities,

$$_k\Delta_a = \frac{k}{a}\delta_a; \qquad _k\Delta_b = \frac{k}{b}\delta_b; \qquad _k\Delta_x = \frac{\delta_x}{abt}.$$

Hence,

$$_t\Delta_t/k = \delta_t/t; \qquad _k\Delta_a/k = \delta_a/a; \qquad _t\Delta_b/k = \delta_b/b;$$

$$_k\Delta_x/k = \delta_x/x\left(\frac{x}{abkt}\right) = \delta_x/x\text{ (approximately)}.$$

From this we conclude that a percentage error in any one of the quantities t, a, b, and x produces the same percentage error in k, the final result. In all measurements of rate of reaction, the formula used for calculating the velocity constant should be examined in this manner so that the effect on the final result of an error in one of the directly measured quantities may be found; the importance of this may be realized by considering the equation for a bimolecular reaction

$$k_2 = \frac{1}{t(a-b)}ln\frac{b(a-x)}{a(b-x)}.$$

When a and b approach each other in value, a small error in either of them becomes greatly magnified in the result: this may be avoided by selecting widely different concentrations of the reactants or by having the initial concentrations equal when the equation becomes

$$k_2 = \frac{x}{at(a-x)}.$$

In the reaction between acetone and iodine, the precision of k, the final result, depends upon the errors of certain direct measurements, which are (1) two titrations of iodine from which the value of x is obtained, (2) measurement of the time t during which x molecules of iodine reacted per liter, (3) measurement of a, the initial concentration of acetone, (5) measurement of the temperature of the reaction. Volatility of one or more of the reactants is perhaps the commonest source of error in measurements of rate of reaction, and affects, in this reaction, the concentration of the iodine and the concentration of the acetone; this error is likely to be appreciable in the ordinary procedure for measuring rate of reaction which consists in withdrawing successive portions of the reaction mixture from a flask and estimating one of the constituents; the space above the liquid becomes saturated with the volatile reactants and part of the vapors diffuse away when the flask is opened to withdraw samples. When one of the reactants is a volatile organic substance which is only slightly soluble in water, the vapor pressure of the aqueous solution will approach that of the pure substance and volatilization losses will be correspondingly great, these are probably the cause of the poor agreement obtained when measuring rate of reaction, using the ordinary technique. Perhaps the best procedure for avoiding this loss is that described in a paper [1] on the estimation of iodine; the reacting solution is made up as usual, but is then transferred by means of a fast running siphon to a number of smaller flasks which are each filled with the reacting solution; loss of the reactants by volatilization is thereby entirely prevented.

Suppose that we wish to measure the rate of reaction between acetone and iodine with an error not greater than 1 per cent, the total error in k caused by the errors in x, t, a, b and in the measurement of the temperature of the reaction mixture must not be greater than $\pm$ 1 per cent. In certain of these measurements it will be possible without any great difficulty to reduce the error so that it is less than 0.33 per cent, in which case, following the usual rule, the effect on the final result may be neglected; it is possible to determine the initial concentration of the acetone and the initial concentration of the acid to within 0.33 per cent without much difficulty; the temperature coefficient of the reaction is such that a change in temperature of 0.01° for the whole time of the reaction changes the velocity 0.13 per cent, so that if the temperature of the thermostat is regulated to $\pm$ 0.02° the temperature error would be negligible: in measuring the time there are two errors, one in measuring the initial time and one in measuring the final time, which are probably not greater than $\pm$ 5 seconds in each case so that the total error in t is $\sqrt{5^2 + 5^2} = 7$ seconds; therefore if the error in t is to be less than 0.3 per cent, an experiment should extend over a minimum time of 40 minutes. It remains therefore to measure x to $\pm$ 1 per cent; all the other errors can then be neglected and the error in k will be $\pm$ 1 per cent; if volumetric apparatus is used it will not be possible to measure x much more accurately than this because x is obtained by taking the difference of two iodine titrations in which the iodine must be estimated much more accurately than $\pm$ 1 per cent, depending on the amount of iodine that reacts. Finally, when measuring rate of reaction the materials used must be purified rigorously since small quantities of highly reactive impurities would cause large errors; simple distillation is usually not sufficient and "chemical" methods of purification should be used whenever possible. In the reaction under consideration it should not be necessary to purify the iodine or the hydrochloric acid if the highest commercial grades are used; the acetone requires special purification which may be by the ordinary bisulfite method or by sodium iodide; [2] acetone or other saturated ketones will not perceptibly decolorize a dilute aqueous solution of potassium permanganate in ten minutes and will not liberate iodine from a solution of hydriodic acid; if the ketone used has the correct boiling point and meets these tests, it is unlikely that it could contain enough impurity to affect appreciably the velocity measurement.

Methods of Measuring Reaction Velocity: There are a number of different methods of measuring velocity of reaction, but, in the most important, the

[1] Rice, Kilpatrick and Lemkin, *J. Am. Chem. Soc.*, **45**, 1361 (1923), see also Price, *Ofvers. af Vet. Akad. Forh.*, **9**, 934 (1899), Slator, *J. Chem. Soc.*, **85**, 1286 (1904).

[2] Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

change of concentration with time of one of the reactants or resultants is measured; it is desirable therefore to classify according to the analytical methods employed. There are however a few methods in which the change of some property of the solution as a whole is used to measure the rate of the reaction. The change in volume which usually accompanies a chemical change was used by Duane [1] to measure the rate of hydrolysis of cane sugar; the solution is kept in a spiral glass tube ending in a graduated capillary tube and the change in volume is measured by the movement of the meniscus along the capillary tube as the reaction progresses: assuming that the volume of the solution is an additive function of the constituents, the changes in volume should be proportional to the quantities of cane sugar left in the solution. The temperature of the thermostat must be very accurately regulated because the volume change of the solution is very small. Benrath [2] measured the change of density of liquid systems during chemical reactions; he obtained fair velocity constants for the following reactions using this method: hydrolysis of cane sugar, hydrolysis of methyl and ethyl acetates, rate of esterification of various acids in alcohols and the rate of hydration of acetic anhydride. Usually the density changes by 1 to 2 parts per 1000 during the course of a reaction so that if the density is measured to about 1 part in 100,000 the deviation of the velocity constant is 1 to 2 per cent.

The change in refractive index has been used to measure rate of reaction by Duane; [3] a photographic method was used, and by assuming that the density and the specific index of refraction are additive functions of the constituents, the rate of hydrolysis of cane sugar is measured.

Dunstan and Mussell [4] showed that viscosity coefficients varied sufficiently in a number of reactions to permit the calculation of the velocity from such measurements.

When the number of molecules changes in the course of a chemical reaction, all those properties depending on the molecular concentrations such as osmotic pressure, rise in boiling point or lowering of freezing point will show a corresponding change. Trevor and Kortright [5] measured the rate of inversion of cane sugar by measuring the change of boiling point of the solution; Kahlenberg, Davis and Fowler [6] made similar measurements using the freezing point lowering of the solution.

Change of Color: In many reactions there is no convenient analytical method for estimating any of the reactants or resultants; in such cases, if one of the reacting substances is highly colored, we have a method for estimating the speed of the reaction which avoids all the difficulties of analytical measurements. Lapworth [7] in a study of the addition of hydrocyanic acid to camphorquinone

[1] *Am. J. Sci.*, 11, 349 (1901); see also Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).

[2] *Z. physik. Chem.*, **67**, 501 (1909).

[3] *Loc. cit.*

[4] *J. Chem. Soc.*, **99**, 565 (1911). See also von Schroeder, *Z. physik. Chem.*, **45**, 75 (1903), and Beck, Trietsche and Ebbinghaus, *Z. physik. Chem.*, **58**, 425 (1907).

[5] *Z. physik. Chem.*, **14**, 149 (1894).

[6] *J. Am. Chem. Soc.*, **31**, 1 (1899).

[7] *J. Chem. Soc.*, **83**, 995 (1903).

states: "It was decided to resort to a method of investigation in which the speed of reaction could be roughly gauged by means of a color change, and for this purpose, advantage was taken of the fact that camphorquinone has a bright yellow color, which is perceptible even in very dilute solutions, whilst its cyanohydrin is almost, if not quite, colorless." A similar method was used by Harcourt [1] in a study of the reduction of ferric chloride by stannous chloride in presence of potassium sulfocyanide; by suitable standards of comparison the rate of fading of the blood-red color and hence the rate of reaction of the ferric ion was measured. When iodine is one of the reactants or resultants, colorimetric observations could also be used to measure the velocity of the reaction. By using an apparatus in which the intensities of two colors could be accurately compared, it is probable that this method could be developed to give results comparable with those obtained by the usual analytical procedure. Edgar and Wakefield [2] used this method to measure the rate of conversion of creatine to creatinine under the influence of hydrochloric acid; at noted time intervals a measured portion of the reaction mixture was taken and neutralized to stop the reaction. The solution was then analyzed for creatinine by Folin's method,[3] which makes use of the red color developed when creatinine is treated with picric acid and sodium hydroxide; a standard solution of creatinine was treated with picric acid and alkali in exactly the same way as the unknown solution, and the color was compared in a Duboscq type of colorimeter; the authors believe that the method gives the concentration of creatinine to $\pm$ 1 per cent.

Optical Rotation: When an optically active substance changes in concentration during the course of a reaction, the polarimeter provides a convenient method of measuring the rate of the reaction. This method has been applied more especially in the study of sugar hydrolysis. A resumé of the work up to 1906 is given by Caldwell,[4] in which it is stated that, up to that time, 140 papers were published on the hydrolysis of cane sugar. The velocity of inversion was first successfully measured by Wilhelmy [5] by means of the polarimeter; since the change in the optical rotation on passing from cane sugar $[\alpha]_D = +66$ to invert sugar $[\alpha]_D = -28$ is so large, accurate measurements may be made with a comparatively rough polarimeter. The technique may be illustrated by the method described in a recent paper.[6]

Polarimeter tubes 40 cm. long were used surrounded by jackets through which water at 25° $\pm$ 0.1 was circulated; 25 cc. of standard hydrochloric acid solution was added to 25 cc. of a 20 per cent solution of sucrose, both solutions being at 25° C., and immediately the mixture was placed in the observation tube; the rotation α_t is noted at convenient time intervals and the final rotation α_∞ is measured after at least 48 hours from the start of the reaction. If we assume that the hydrolysis of cane sugar is represented by some such scheme as the following:

$$C_{12}H_{22}O_{11} + H_2O = C_{12}H_{22}O_{11}.H_2O \quad \text{(Rapid)},$$
$$C_{12}H_{22}O_{11}.H_2O + H^+ = C_6H_{12}O_6 + C_6H_{12}O_6 + H^+ \quad \text{(Slow)},$$

[1] *Phil. Trans.*, **212A**, 187 (1913).
[2] *J. Am. Chem. Soc.*, **45**, 2242 (1923).
[3] Folin, *Am. J. Physiol.*, **13**, 48 (1905).
[4] *Brit. Assoc. Adv. Sci. Rep.*, 351 (1906).
[5] *Pogg. Ann.*, **81**, 413, 499 (1850).

we can conclude that the velocity of the slow reaction will be proportional to the concentration of the cane sugar and to the concentration of the hydrochloric acid, if the reaction takes place in dilute solution. The velocity equation will be, therefore,

$$k_2 = \frac{1}{at} ln \frac{b}{b - x},$$

where a is the initial concentration of the hydrochloric acid which remains constant during the experiment, b is the initial concentration of the cane sugar and $(b - x)$ is its concentration after time t. The ratio $b/(b - x)$ is independent of the particular unit of concentration used so that if the rotations are additive we can replace $b/(b - x)$ by $\frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$, where α_0 is the initial rotation and α_∞ is the final rotation. Rosanoff, Clarke and Sibley [1] showed that the specific rotation of the solution is an additive function of its composition and also gave a method for calculating α_0; a slight error in the value of α_0 will be greatly magnified in the value of k calculated for the earlier stages of the reaction, so instead of trying to obtain α_0 by direct observation they extrapolated to $t = 0$ the straight line obtained by plotting values of t against corresponding values of $\log (\alpha_t - \alpha_\infty)$; this gives far more reliable values of $\log (\alpha_0 - \alpha_\infty)$ than can be obtained by direct measurement.

The optical rotation of mixtures of sugars has been the subject of a number of recent investigations [2]; Hudson has pointed out that strict proportionality between change in rotation and the amount hydrolyzed would be possible only if the specific rotation of sucrose, glucose and fructose does not change with concentration, a condition which is only approximately fulfilled in the case of the pure sugars. Vosburgh notes that for sucrose and glucose the variation is negligible but in the case of fructose it is appreciable in magnitude and the variation is in such a direction as to cause an apparent increase in the velocity coefficients when the latter are calculated by the unimolecular equation, an effect noticed by several observers; on the other hand, Nelson and Beagle found that the specific rotation of fructose is affected by the presence of sucrose, but the effect is in such a direction as to compensate partly for the variation in specific rotation with concentration in the case of the hydrolysis of sucrose. Vosburgh gives a complete discussion of these errors and concludes that the polariscopic determination of the per cent of sucrose replaced by invert sugar gives a velocity constant about 0.4 per cent too high when sodium light is used; by using light of wave-length $\lambda = 546.188$, obtained from a mercury vapor lamp, the error is appreciably less.

Conductivity: When a reaction occurs which involves a change in concentration of an electrolyte, conductivity measurements provide a convenient method of following the course of the reaction. This method has been applied to the measurement of the rate of hydration of acid anhydrides; [3] it is not possible to measure the rates of these reactions by titrating the acid produced by alkali because the reactions are extraordinarily sensitive to traces of alkali.

Previous attempts by Menschutkin and Vasilieff,[4] and by Lumière and Barbier [5] in which other methods were used were unsuccessful and Rivett and Sidgwick state: "We have

[1] *J. Am. Chem. Soc.*, **33**, 1911 (1911).

[2] *J. Am. Chem. Soc.*, **32**, 885 (1910); Nelson and Beagle, *ibid.*, **41**, 572 (1919); Vosburgh, *ibid.*, **43**, 219 (1921).

[3] Rivett and Sidgwick, *J. Chem. Soc.*, **97**, 732, 1677 (1910).

[5] *J. Russ. Phys. Chem. Soc.*, **21**, 188 (1889).

[4] *Bull. Soc. chim.*, **35**, 625 (1906).

endeavored to determine the constant with greater accuracy by means of the conductivity. If we start with a solution of the anhydride in water, the conductivity at any moment is due solely to the amount of acetic acid formed; and the only way in which the presence of the unchanged anhydride is likely to affect it is by its influence on the viscosity of the solution." The only drawback to this method appears to be the somewhat uncertain viscosity correction. Recently Skrabal [1] has devised an ingenious method for measuring the velocity of hydration of acetic anhydride by conducting the reaction in presence of sodium iodide and iodate, the acetic acid liberating an equivalent quantity of iodine which can be estimated in the usual way. By having thiosulfate and starch present, the change of color when all the thiosulfate had reacted could be used for measuring the velocity.

Walker [2] has used conductivity measurements for measuring the rate of hydrolysis of esters by caustic alkalis.

"The chief conditions for the convenient application of the method are: first, that there should be a considerable difference in conductivity between the initial and final systems, and second, that the change in conductivity should be proportional to the progress of the reaction. It occurred to me that these conditions would be well fulfilled in the saponification of an ester by a caustic alkali. The conductivity of the alkali, say sodium hydroxide, is much greater than that of the sodium salt produced by the saponification, owing to the high velocity of hydroxide ion as compared with the salt anion. Since, too, sodium hydroxide and sodium salts of monobasic acids are approximately equally ionized under the same conditions, the ionization in dilute solution remains practically the same throughout the saponification, and thus the alteration in the conductivity is almost exactly proportional to the progress of the reaction."

Measurements of the hydrolysis of methyl acetate and ethyl acetate by sodium hydroxide gave constants, the maximum deviation of which from the mean value in any series was less than 2 per cent; further, the results agreed with those obtained by Warder [3] and by Reicher.[4] Walker and Kay [5] used conductivity measurements to follow the rate of decomposition of ammonium cyanate in dilute aqueous solution; the equation representing the change is

$$NH_4^+ + CNO^- = CO(NH_2)_2.$$

Other workers [6] have also used the conductivity method.

Gas Evolution: The measurement of velocity of reaction by the rate of gas evolution has been carefully studied by a number of workers. Recently Harned [7] has studied the catalytic decomposition of hydrogen peroxide by the iodide ion; measurements of the amount of oxygen evolved after definite time intervals gave the necessary data for calculating the velocity constant. It is necessary to agitate the solution to prevent supersaturation with the oxygen formed in the decomposition and this is done by means of a rapidly revolving glass stirrer sealed from the outside by the well-known mercury seal method; [8] since the stirrer is rotated between 1000 to 1500 revolutions per

[1] *Monatsh.*, **43**, 493 (1923).
[2] *Proc. Roy. Soc.*, **78A**, 157 (1906).
[3] *Am. Chem. J.*, **3**, 203 (1881).
[4] *Liebig. Ann.*, **228**, 257 (1885); *ibid.*, **232**, 103 (1886).
[5] *J. Chem. Soc.*, **71**, 489 (1897).
[6] Cohen and Kaiser, *Z. physik. Chem.*, **89**, 357 (1915).
[7] *J. Am. Chem. Soc.*, **40**, 1461 (1918).
[8] See also Holn and Greenbank, *J. Ind. Eng. Chem.*, **15**, 1134 (1923).

minute, the apparatus must be carefully constructed, but it has the advantage that it could be used for any type of reaction in which a relatively insoluble gas is evolved. Preliminary experiments showed that, when there was no iodide ion present, the decomposition of the hydrogen peroxide by the stirring apparatus was negligible; excellent results were obtained and the results of experiments could be duplicated to within ± 1 per cent. Francis and his co-workers [1] have used this method to investigate the decomposition of nitrosotriacetonamine by alkalis into phorone and nitrogen; the following equation represents the reaction:

$$\begin{matrix} \diagup CH_2.C(CH_3)\diagdown \\ CO \qquad\qquad N.NO \\ \diagdown CH_2.C(CH_3)\diagup \end{matrix} + OH^- = H_2O + N_2 + CO \begin{matrix} \diagup CH:CCH_3 \\ \qquad\qquad + OH^-. \\ \diagdown CH:CCH_3 \end{matrix}$$

In their later work they designed a special apparatus in which the pressure of the evolved nitrogen was measured; this gave a much higher degree of accuracy without lengthening the time of an experiment. A list of other publications in which gas evolution is used to measure reaction rates is given below.[2]

Acidimetry and Alkalimetry: These methods are commonly used in the study of hydrolytic reactions and may be illustrated by the hydrolysis of methyl acetate by hydrochloric acid.

The original method devised by Ostwald [3] for measuring the velocity has been used by most investigators with slight modifications; a known amount of standard hydrochloric acid is added to a small flask and then sufficient water so that when the ester is added, the total volume is 50 cc.; the flask is then placed in the thermostat for thirty minutes, and the required amount of ester added at a noted time; thus, for each experiment, the concentration of each constituent is known. From time to time 2 cc. portions of the solution are withdrawn by means of a pipette and added to about 40 cc. of water and the total acid estimated by standard baryta; the deviation of measurements made by this method is probably 2–3 per cent. A similar procedure was followed by Reicher [4] in a careful study of the rate of hydrolysis of esters by alkalis; measured portions of the solution were added to standard sulfuric acid and the excess acid determined by titration with baryta water.

Iodimetry: The application of iodimetry in the study of rate of reaction may be illustrated by the isomeric change of acetyl-chloro-amino-benzene to *p*-chloro-acetanilide under the influence of hydrogen ions and chloride ions [5]; the course of the reaction was followed by adding a measured quantity of the reacting solution at definite time intervals to a solution containing an excess of

[1] Clibbins and Francis, *J. Chem. Soc.*, **101**, 2358 (1912); Francis and Geake, *ibid.*, **103**, 1722 (1913); Francis, Geake and Roche, *ibid.*, **107**, 1651 (1915).

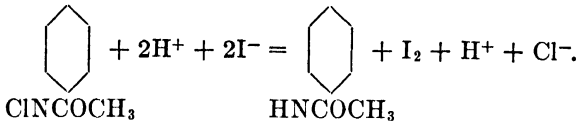
[2] Lamplough, *Proc. Camb. Phil. Soc.*, **14**, 580 (1908); Walton, *Z. physik. Chem.*, **47**, 185 (1904); Fraenkel, *ibid.*, **60**, 202 (1912).

[3] Ostwald, *J. prakt. Chem.*, **28**, 449 (1883).

[4] *Ann.*, **228**, 257 (1885).

[5] Rivett, *Z. physik. Chem.*, **82**, 201 (1913).

potassium iodide. The following reaction takes place:



The *p*-chloro-acetanilide does not react with the iodide. The free iodine is then titrated with standard sodium thiosulfate using starch as indicator. Lapworth [1] studied the rate of addition of chlorine and bromine to acetone under the catalytic influence of various acids; here, the reaction may be followed by adding a measured quantity of the reacting solution to a neutral buffer containing an excess of potassium iodide; the buffer solution stops the reaction and the chlorine or bromine liberates iodine in equivalent quantity which may then be estimated by standard thiosulfate.

Measurement of Very Rapid Reactions: [2] In connection with the measurement of velocity of reaction there are in general two problems: (1) To arrange that the chemical system under investigation be made initially unstable in a period of time that is negligibly short in comparison with that taken by the chemical reaction. (2) To record from time to time the points reached by the unstable system by means of methods which take a negligibly short time in comparison with that taken by the chemical reaction. In the case of slow reactions both these requirements can easily be met, for the initially unstable system can be made by mixing the reactants, an operation which takes only a few seconds; this can be neglected if the reaction takes many minutes or hours to reach equilibrium. Since the dynamical study of slow reactions has thrown so much light upon the general mechanism of chemical reactions, the value of a method for measuring the velocity of rapid reactions can hardly be questioned; however, in the case of reactions so rapid that equilibrium is reached within perhaps a second, the methods used for slow reactions break down completely, and it is necessary to search for new modes of attack. In one method, the initial unstable condition was obtained by passing light through a system photochemically reversible; by cutting off the light, the concentrations of the reactants return to their previous dark values. The procedure used is to pass the solution through a tube, a section of which is exposed to a strong beam of light (which displaces the system from its dark equilibrium); sections of the tube further along are then examined by a suitable optical method to obtain the concentrations of the reactants at these points. This method was not developed because comparatively few reactions are photochemically reversible and in addition there is the uncertainty as to whether the effects of the light upon the system disappear at the instant at which the light beam is interrupted. Instead, a mixing process was devised which can be completed before any appreciable degree of chemical action can

[1] *J. Chem. Soc.*, **85**, 30 (1904).

[2] Hartridge and Roughton, *Proc. Roy. Soc.*, **104A**, 376 (1923).

take place. The principle of the method consists in causing the fluids to be mixed to come together at a high velocity within a special type of mixing chamber; the two streams of fluid having met one another and mixed very completely then pass down an observation tube and at measured points the concentrations of the reactants are determined by a suitable optical method, which may involve measurements of (*a*) opacity, (*b*) color, (*c*) absorption in definite spectral regions, (*d*) wave-length of absorption bands, (*e*) rotation of the plane of polarization, (*f*) refractive index. The necessary time measurements are obtained from a knowledge of the rate of flow down the observation tube and the distance between the cross-sections where determinations are made. Hartridge and Roughton find [1] that the velocities of reactions with a half period of only 0.03 sec. may be measured by this method; they have applied the method to the measurement of the rate at which oxygen dissociates from its combination with hæmoglobin.

Measurement of Temperature Coefficients: This is usually done by measuring the velocity at two temperatures, the ratio giving a measure of the effect of temperature on the velocity; the method however is laborious and time-consuming, for it requires two separate exact experiments; also, the error in the temperature coefficient is much greater than in a single velocity measurement being given by $\sqrt{e_1^2 + e_2^2}$ where e_1 and e_2 are the errors of the two velocity measurements. Recently a method for measuring temperature coefficients has been devised [2] which requires only one experiment and gives a high degree of precision in the result. The principle of the method is shown by the following description of the procedure followed when measuring the temperature coefficient of the reaction between acetone and iodine in aqueous solution.

"We had two thermostats working side by side, one at t_1 and the other at t_2, and each regulated to $\pm$ 0.003°. We filled a liter bottle with a solution of acid and iodine of approximately the strengths used in a velocity determination. The bottle was then filled with a titrating siphon and the iodine accurately estimated in the usual manner with thiosulfate. After removing the siphon, we weighed the bottle and contents and, by subtracting the weight of the empty bottle, we obtained the weight of the solution. We then placed the bottle in the thermostat of lower temperature (t_1), and when it had attained this temperature we started the reaction by running in the required quantity of acetone from a pipet, immediately agitated the bottle, fitted it with a quick-running siphon and filled four 100 cc. glass-stoppered reaction tubes with the solution. Two of the tubes were placed in the thermostat at t_1, and two in the other thermostat. We noted carefully the time at which we added the acetone and also the time at which the two tubes were placed in the thermostat at t_2. After a suitable time, usually 3–4 hours, we fitted the tubes with a titrating siphon and determined the iodine as in a velocity experiment. From these data we could obtain the rate of loss of iodine in each set of tubes expressed in terms of cc. of thiosulfate per minute. No correction is necessary for the results at t_1, since the tubes were at this temperature all the time. A small correction is necessary for the results obtained at t_2, since the reacting solution was at t_1 for a short time (usually 2 minutes) and also the solution took some time to attain the temperature t_2 after being transferred to the bath of higher temperature. A further correction is necessary because the solution diminished in density when raised to the higher temperature. The total of these corrections, however, is very small and amounts usually to less than 1 per cent."

[1] *Ibid.*, **104A**, 396 (1923).

[2] Rice and Kilpatrick, *J. Am. Chem. Soc.*, **45**, 1410 (1923).

It is evident that the ratios of the corrected rates of loss of iodine at the two temperatures gives the temperature coefficient of the reaction; these rates may be expressed in terms of cc. of thiosulfate per minute, so that it is not necessary even to standardize the thiosulfate. Temperature coefficients determined in this manner agree with those determined from the results of two separate experiments.

Theoretical

The rapid increase of the rate of reaction with temperature is one of the outstanding difficulties in the theoretical treatment of this subject; there are a few reactions which show only a slight increase of velocity with temperature; Slator [1] showed that there is practically no reaction in a dilute solution of chlorine in benzene, but, in presence of a trace of iodine chloride, chlorobenzene and benzene hexachloride are formed at measurable rates; the value of k_{25}/k_{15} is 1.05 where k is the rate of disappearance of chlorine. Dushman [2] and also Skrabal [3] have studied the rate of formation of free iodine from the iodide ion and the iodate ion, another reaction which has a very small temperature coefficient; photochemical reactions usually have small temperature coefficients. However, with ordinary chemical reactions which proceed with measurable velocity, such behavior is quite exceptional and the increase in velocity per 10° rise in temperature is usually from 200 to 400 per cent. On kinetic considerations we can account for a 2–3 per cent increase in velocity for a 10° rise in temperature, because the rise in temperature will increase the velocity of the reacting molecules and diminish the viscosity of the solvent; for reactions of a low order these influences probably tend to increase the rate of collision of the reacting molecules, but, for more complicated reactions, the rate of collision may actually be diminished; there appears to be little hope of accounting for the temperature coefficients of chemical reactions on the basis of kinetic theory.

There is also another difficulty quite as great in connection with reaction rates. A mixture of iodine and sodium thiosulfate even in the most dilute solution, say 0.00001 N, reacts practically instantaneously and the same is true of a mixture of barium chloride and silver sulfate in very dilute solution; a very great number of such "instantaneous" reactions are known. If, however, we make up a solution of acetone, iodine and acid such that the concentrations of the reacting molecules are: 0.1 M acetone, 0.1 N hydrogen ion and 0.01 N iodine, we find that this reaction goes at a very slow rate and takes over an hour for one half of the reactants to disappear. From experiments with such reactions as that between iodine and sodium thiosulfate, it follows that, even at concentrations as low as 0.00001 N, the number of molecular collisions is sufficient to permit a reaction to be practically instantaneous; we are forced to conclude, therefore, that, in slow reactions, only a very small proportion

[1] *J. Chem. Soc.*, **83**, 729 (1903).
[2] *J. Phys. Chem.*, **8**, 453 (1904).
[3] *Monatsh.*, **32**, 815 (1911).

of the collisions result in chemical interaction or else the reaction occurring in the solution is not that represented by the stoichiometric equation of the change. It is of course possible that reacting molecules may have to collide at definite portions of their surfaces,[1] and it is conceivable that, in the special case of reactions between complicated organic compounds, this factor might account for the existence of slow reactions; however, it is hardly possible that it is a general explanation.

Another difficulty [2] will be realized by considering a reaction between two different molecules A and B; ordinarily, we state that the velocity of the reaction is proportional to the product of the concentrations of A and B, which postulates that the rate of the reaction simply depends on the probability of A and B coming into contact with one another. If, however, the velocity depended only on the probability of collision, we might expect the velocity to be independent of the specific nature of the reactants, and to be determined simply by the temperature, the mean free path, and the speed of the molecules; owing to the highly specific nature of reaction velocity, it is evident that reactivity depends on other factors as well. The hypotheses which have been put forward to meet these difficulties will now be considered.

The Arrhenius Hypothesis: Most of the explanations for the high temperature coefficients of chemical reactions usually center around the empirical equation of Arrhenius [3] connecting velocity of reaction and temperature, which may be written

$$\frac{d\ln k}{dT} = \frac{Q}{RT^2},$$

where Q is a constant. Arrhenius traced a relation between the variation of an equilibrium constant with temperature and the variation of the reaction velocity with temperature. Consider the equilibrium $B + C \rightleftarrows A$; we then have

$$K = \frac{[A]}{[B] \times [C]},$$

where K is the equilibrium constant and $[A]$, $[B]$ and $[C]$ are the equilibrium concentrations of A, B and C respectively at the temperature t. The equilibrium constant K will vary with the temperature and this variation will depend on the heat of the reaction $B + C = A$; the relation is given by the van't Hoff isochore,

$$\frac{d\ln K}{dT} = \frac{Q}{RT^2},$$

[1] See Stern, *Ann. Physik.*, **44**, 497 (1914); Dushman, *J. Am. Chem. Soc.*, **43**, 397 (1921); Bjerrum, *Z. physik. Chem.*, **108**, 87 (1924).

[2] See Lewis, *Brit. Assoc. Adv. Sci. Rep.*, 394 (1915).

[3] *Z. physik. Chem.*, **4**, 226 (1889).

which in the integrated form is

$$ln \frac{K_1}{K_2} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where Q is the heat of the reaction. We can readily calculate that if the reaction absorbs, say, 20,000 cal. per mole of A produced, then the ratio of the equilibrium constants at 35° and 25°, $K_{35}/K_{25} = 3.1$ (approximately); the equilibrium constant varies rapidly with the temperature if the heat of the reaction is high. The next step is to consider a special case of the equilibrium, namely, when the equilibrium concentration of A is very small; it will be readily seen that the equilibrium concentrations of B and C will not vary appreciably with change in temperature so that we can write $K \propto [A]$, and, therefore,

$$K_{35}/K_{25} = [A]_{35}/[A]_{25} = 3.1.$$

Considering the hydrolysis of cane sugar by hydrochloric acid in aqueous solution, Arrhenius suggested that the cane sugar is present in two forms, active and inactive, in mass action equilibrium; the equilibrium concentration of the active form is supposed to be very minute and to be attained practically instantaneously; if K is the equilibrium constant of the reaction active $\rightarrow$ inactive cane sugar molecules, we can evidently write as before

$$K_{35}/K_{25} = [A]_{35}/[A]_{25};$$

Arrhenius postulates that only the active molecules undergo hydrolysis and that the high temperature coefficient of the reaction is due almost wholly to the increase in concentration of the active molecules; k_{35}/k_{25} for this reaction is approximately 4 which is also the value for $[A]_{35}/[A]_{25}$, so that we can calculate that the heat of the reaction

$$\text{active cane sugar} \rightarrow \text{passive cane sugar}$$

is 26,000 cal. per mole. Other temperature coefficients for other reactions would correspond to other heats of transformation from inactive to active molecules; for the reaction between acetone and iodine the acetone would be considered the active molecule and in the solution we would have the equilibrium

$$\text{acetone (inactive)} \rightleftharpoons \text{acetone (active)};$$

since the value of k_{35}/k_{25} is approximately 3, the heat of transformation from inactive to active acetone molecule is approximately 20,000 cal. The temperature coefficient of the hydrolysis of ethyl acetate is $k_{35}/k_{25} = 2.5$ so that the heat of transformation from inactive to active ethyl acetate molecule is 16,500 cal. (approximately). Arrhenius further extended this hypothesis to explain catalysis by assuming that the hydrogen ion or other catalyst shifts the equilibrium to the active side and therefore increases the velocity of the reaction.

Several objections to this hypothesis are immediately apparent; the assumption that the catalyst increases the rate of a reaction by shifting the equilibrium between the active and inactive molecules is contrary to one of the conceptions of catalytic activity, which is that a catalyst does not affect the equilibrium point of a reaction in dilute solution; further, the assumption that substances like cane sugar, ethyl acetate, etc., exist in two forms in solution is very artificial and is without experimental support; indeed, when considering multimolecular reactions we have nothing to guide us when selecting the reactant which is supposed to be present in two forms. For the reaction between cane sugar and water catalyzed by hydrogen ion, we might select any one of the three entities taking part in the reaction and by saying that it was present in two forms, active and inactive, we could deduce the Arrhenius empirical equation; there would perhaps be some justification for saying that the water exists in two forms, active and passive, for liquid water is ordinarily supposed to be a mixture of simple water molecules with various polymers; we might therefore postulate that the simple water molecules are present in very minute concentration and are the active molecules in the hydrolysis. This would account for the high temperature coefficients of hydrolytic reactions but it would also follow on the basis of this hypothesis that all hydrolytic reactions would have the same temperature coefficient; since this is not the case we cannot derive the empirical Arrhenius equation by postulating that the water is present in two forms. The remaining possibility that the hydrogen ion exists in two forms will be considered later.

The Arrhenius hypothesis can hardly be regarded as anything more than an *ad hoc* explanation of the difficulty; from it we can conclude that each chemical reaction has a unique temperature coefficient depending on the heat of activation of the active molecules of the substrat but there does not seem to be any way of developing the hypothesis so that it can be tested.

The Radiation Hypothesis: The method of development of the radiation theory is similar to the method of development of the Arrhenius hypothesis; the usual process used by investigators has been to make up a set of postulates which enable them to deduce an equation of the same form as the Arrhenius empirical equation, and on these postulates to develop a theory of chemical reactivity. Trautz,[1] who first suggested that ordinary reactions are produced by infra-red light, took as his fundamental assumption that a molecule must be in an active state in order to react; if Q is the heat of activation and α is the fraction of the molecules which at any temperature T possess this energy, he deduced the equation

$$\frac{d\ln\alpha}{dT} = \frac{Q}{RT^2}.$$

In this manner, by assuming that only a definite fraction of each type of molecule is capable of reacting at any given temperature he showed that the rate of a bimolecular reaction in gases may be calculated from the frequency of

[1] *Z. wiss. Photochem.*, **4**, 160 (1906).

collisions between the active molecules as deduced from kinetic theory considerations. Marcelin [1] assumes that the internal energy of the molecules varies in conformity to the laws of statistical mechanics, and that a spontaneous transformation or reaction is produced when the internal energy attains a certain critical value; on this theory therefore it is not the number of activated molecules present at any instant which determines the rate of the reaction, but the rate at which the molecules acquire this critical energy; he deduces the equation

$$dlnk/dt = E/RT^2,$$

where E may be called the critical increment, that is, the energy absorbed by the molecule, in excess of the average energy possessed by all the molecules, before it becomes reactive. The above equation is of the same form as the empirical equation of Arrhenius.

It is evident therefore that, from quite different and mutually exclusive assumptions, the empirical equation of Arrhenius may be developed; the deduction of this equation from any set of propositions does not justify us in referring to such propositions as anything more than speculation or at best a hypothesis [2]; it is an experimental fact that the velocity of reaction increases with rise in temperature and that the temperature coefficient diminishes with rise in temperature; this is sometimes quoted as evidence of the correctness of one or other of these hypotheses, but actually it proves nothing more than that reactions follow the empirical Arrhenius equation, which, written in the form

$$\frac{1}{k}\frac{dk}{dT} = \frac{Q}{RT^2},$$

states plainly that the temperature coefficient of a chemical reaction is inversely proportional to the square of the absolute temperature. The development of one of these hypotheses by the application of the concept that radiation plays an essential part in chemistry was made by W. C. McC. Lewis [3] and later, though independently, by Perrin.[4]

As pointed out by Perrin, the existence of such reactions as $A_2 \rightleftharpoons 2A$ shows the necessity of considering some agent besides molecular collisions. On the

[1] *Ann. phys.*, 3, 120 (1915); *idem*, *Compt. Rend.*, 158, 161 (1914).

[2] It may be noted that the method used in deducing the Arrhenius equation has been questioned in certain cases. Perrin, *Trans. Farad. Soc.*, 17, 555 (1922), states: "Trautz . . . has developed ideas which are certainly cognate (but which I have not quite understood) and to which I would refer the reader." Tolman (*J. Am. Chem. Soc.*, 44, 76 (1922)) states: "Thus Marcelin, in his important contribution to the theory of physical kinetics (*Ann. Phys.*, 3, 120 (1915)), has made use of a relation between free energy and a quantity occurring in the Maxwell-Boltzmann distribution law which the present writer believes to be incorrect. An article attempting to justify Marcelin's procedure has recently been published by E. P. Adams (*J. Am. Chem. Soc.*, 43, 1251 (1921)) but the present writer cannot agree with Adams's conclusions."

[3] Lewis and co-workers, *J. Chem. Soc.*, 1914–1923.

[4] Perrin, *Ann. phys.*, 11, 1 (1919).

molecular scale this reaction consists in the sudden appearance of a molecular grouping $2A$ at a spot where there was the group A_2; when we consider that the fraction of A_2 dissociating at any instant at any given temperature is independent of the actual number of molecules of A_2 present in unit volume we must conclude that the probability that a molecule of A_2 will dissociate is independent of the number of collisions with other molecules and must consequently depend upon some process occurring within the structure of the molecule itself. Perrin concludes that the agent which can break up and remake a molecule, even in a vacuum where there are no collisions and make it conform to temperature, is the same which imposes a definite temperature upon a thermometer suspended in a vacuum; it is, in the most general sense of the word, radiation, isothermal under stationary conditions, which fills the enclosure at each instant and in which the molecule remains immersed.

Lewis [1] takes as his initial assumption that temperature effect must be due to some influence on, or connected with, the internal structure of the molecules taking part in the reaction, since the increase in velocity cannot be explained from the mere increase in kinetic movement; further, he assumes that the same influence underlies the phenomenon of catalysis in homogeneous solution so that catalysis is due to some influence on, or connected with, the structure of the molecules. He concludes: "Owing to the generality and comparability of catalysis in homogeneous solutions, as, for example, the approximate proportionality between the velocity of the reaction and the concentration of the catalyst on the one hand, and the generality of the temperature coefficient which is of the same order for a whole series of widely varying reactions, on the other hand, one is tempted to seek for some physical basis which would apply equally to both." He then adopts the Trautz conception that ordinary chemical reactions are due to infra-red radiation and suggests that the mechanism of homogeneous catalysis is essentially the absorption by the reactants of infra-red radiation emitted by the catalyst; when the internal energy of a molecule reaches a certain critical value it becomes chemically reactive; since any system will have a normal radiation density in virtue of its temperature, this may happen in the absence of a catalyst, its only function being to increase the density of the particular kind of infra-red radiation absorbed by the reactants. The effect of temperature on the other hand is to increase the total infra-red radiation density throughout the system, and therefore increase those particular regions which the substance is capable of absorbing. This is the material mechanism supposed to underlie the transformations considered by Marcelin; the critical increment E, that is, the excess energy over the average possessed by a molecule necessary to bring it to the chemically active condition, is supposed to be obtained by absorption of infra-red energy of a particular wave-length by the reactants.

Measurements of the rate of hydrolysis of sucrose [2] over the range 25° to 35° show that $k_{35}/k_{25} = 4.13$; substituting this in the integrated form of the

[1] Lamble and Lewis, *J. Chem. Soc.*, **105**, 2330 (1914).

[2] Lamble and Lewis, *J. Chem. Soc.*, **107**, 233 (1915).

Marcelin equation

$$ln\frac{k_{35}}{k_{25}} = \frac{E}{R}\left(\frac{1}{298} - \frac{1}{308}\right)$$

we obtain for E the value 26,000 cal. per mole; dividing this by the Avogadro number and converting into ergs we obtain 1.6×10^{-12} ergs for the amount of energy above the average necessary to activate a single molecule of sugar. The next step is to introduce the important idea of the quantum, which allows us to state that when radiation of frequency ν causes a molecule, isolated in space, to pass from one stationary state to another stationary state, the internal energy of this molecule is increased by the quantum $h\nu$, where h is Planck's constant (6.55×10^{-27} ergs/sec.); equating $h\nu$ to E per molecule we obtain $\nu = 1.6 \times 10^{-12}/6.55 \times 10^{-27} = 2.44 \times 10^{14}$. The wave-length corresponding with this is 1.23×10^{-4} cm., or 1.23 μ which is in the short infra-red region in which sucrose shows strong absorption; this earlier work has been confirmed and extended by more complete studies [1] of the reaction. Perrin commenting on these calculations states: "The result appears very satisfactory and remarkable even, because we might have obtained altogether unreasonable values of any order of magnitude, if the theory were arbitrary." The infra-red absorption spectrum of triethyl sulphine bromide was measured [2] in various solvents; from the measurements of von Halban [3] on its rate of decomposition in these solvents, the critical increment and hence the characteristic frequency of the substance in each solvent could be obtained; comparison of the observed and calculated frequencies showed close agreement in most cases.

The view that radiation is the ultimate source of all energy which makes chemical reactivity possible is developed by Lewis and his co-workers in a series of papers from 1914 onward; the basis of the view is that the rate of a unimolecular reaction is identical with the number of molecules which attain the critical state per second; in a bimolecular reaction however where two molecules are simultaneously concerned it is necessary that each reacting species attain the critical energy before reaction can take place. Active molecules in unimolecular processes have therefore no real existence, but in multimolecular reactions it is conceivable that active molecules exist, the rate of the observed reaction depending on the number of collisions per second which take place between active molecules of the reactants. Lewis concludes also that the equilibrium between active and passive molecules is attained practically instantaneously; his calculations show that the proportion of chemically effective collisions is an exceedingly small fraction of the total number of collisions in the same time; this fraction is referred to as the chemical efficiency of the reaction and increases very rapidly with the temperature.

[1] Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920); Moran and Lewis, *ibid.*, **121**, 1618 (1922).

[2] H. A. Taylor and Lewis, *J. Chem. Soc.*, **121**, 665 (1922).

[3] *Z. physik. Chem.*, **77**, 129 (1909).

Lewis [1] has shown that combining these considerations with the kinetic theory, we may calculate the number of collisions per cc. per second between active molecules and hence obtain the velocity of a bimolecular gas reaction; the observed and calculated rates are of the same order for several different reactions, which is satisfactory agreement because the expression giving the rate of collision of molecules contains a term involving the square of the distance within which two molecules approach one another during a collision and nothing is known of this term beyond the fact that it is of the order of magnitude of the diameter of a molecule.

A recent discussion [2] of the radiation theory of chemical reaction showed that there was considerable divergence of views amongst chemists; a number of objections to the radiation theory were brought forward and these were met in such an unconvincing manner that it would appear that the radiation theory at any rate in its present form is not satisfactory. Lowry pointed out that the two examples of unimolecular reactions selected by Perrin were really pseudo-unimolecular; that the first case selected, namely the dissociation of gases, requires the presence of water vapor or a catalyst and that the second case, one of isomeric change, also requires the presence of a catalyst; he concludes:

"My own experiments on nitrocamphor have shown that even the extraordinarily facile isomeric change which this compound undergoes can be arrested by eliminating the minute trace of catalyst on which it ordinarily depends. How minute this quantity is may be judged from the fact that a notable acceleration in the velocity of isomeric change is effected by the addition of a single decigram of piperidine to a ton of benzene. From these and other similar observations, it is probable that even the slight molecular rearrangement which is involved in the wandering of a mobile hydrogen atom can only be effected by the aid of other molecules having active catalytic properties."

In replying to this, Perrin admitted that many reactions considered unimolecular are really bimolecular but continued:

"On the other hand, novel unimolecular reactions might have to be taken into consideration, such as the dissociation of a complex intermediate molecule, formed by the catalyst and one of the products of the reaction. I should add here, though the remark may appear obvious, that we cannot assume that every reaction requires a chemical catalyst. Otherwise we should have to imagine a second catalyst for the intermediate reactions in which the first catalyst plays a part, and so on, to infinity."

On the basis of the radiation hypothesis unimolecular chemical reactions have a special interest as distinct from reactions of a higher order. The observed rate of a bimolecular reaction is determined only by the rate of collision of activated molecules since it is assumed that the primary process of activation is very rapid; on the other hand, the rate of a unimolecular reaction is determined by the rate of interaction of the molecules and the radiation since collisions can play no part in the reaction. The early attempts to calculate the velocity of a unimolecular reaction gave results far removed

[1] *J. Chem. Soc.*, **113**, 471 (1918).
[2] *Trans. Farad. Soc.*, **17**, 546 (1922).

from the observed values and a somewhat extensive literature [1] has grown up dealing with the theoretical aspect of unimolecular reactions. It must be admitted however that the theory of unimolecular chemical reactions can scarcely be regarded as placed on a sound basis until unequivocal examples of such reactions have been found. Practically all those reactions which might at first sight be considered unimolecular have proved on investigation to be multimolecular or to be catalyzed by the walls of the vessel: the thermal decomposition of ozone [2] is homogeneous but bimolecular; the thermal decompositions of chlorine monoxide and of phosgene [3] at high temperatures are homogeneous reactions but the rates depend on the pressure in such a way as to show that collision effects determine the rates and therefore the reactions are multimolecular; the thermal decomposition of nitrogen pentoxide which appeared to be an example of a unimolecular change has now been shown to be at least bimolecular, small traces of the decomposition products being necessary to secure a constant specific rate of decomposition [4]; hydrogen peroxide and sulfuryl chloride [5] decompose thermally and these have been shown to be typical heterogeneous reactions taking place on the walls of the containing vessel; the possible exception of the thermal decomposition of phosphine [6] at high temperatures has now been shown to be a "wall" reaction at the surface of the containing vessel.[7] Such gas reactions, therefore, proceed as homogeneous multimolecular reactions or are catalyzed by the walls of the vessel. It would be the strongest possible argument in favor of the radiation hypothesis if we had even a single example of a chemical reaction which proceeds with measurable speed and which we were reasonably certain was a true unimolecular reaction.

Lindemann brought forward the objection that if reaction velocity is proportional to radiation density of a given wave-length then the inversion of sucrose which has a temperature coefficient of 4.13 for 10° must be determined by the radiation density of wave-length 1.058 μ; the radiation density of this wave-length is 5×10^{13} times greater in sunlight than in the dark, yet the reaction proceeds at approximately the same rate. Perrin attempted to meet this difficulty by assuming that the frequency ν calculated from the constant of Arrhenius may be the sum $\nu_1 + \nu_2 + \cdots$ of the really active frequencies; the

[1] Lewis, *Phil. Mag.*, **34**, 26 (1920); Rideal, *ibid.*, **40**, 461 (1920); Langmuir, *J. Am. Chem. Soc.*, **42**, 2190 (1920); Polanyi, *Z. physik.*, **3**, 31 (1920); Tolman, *J. Am. Chem. Soc.*, **43**, 269 (1921); Dushman, *ibid.*, **43**, 397 (1921); Lewis and McKeown, *ibid.*, **43**, 1297 (1921); Rodebush, *ibid.*, **45**, 606 (1923); Christiansen, *Z. physik. Chem.*, **103**, 91 (1922); J. Rice, *Phil. Mag.*, **46**, 312 (1923); McKeown, *ibid.*, **46**, 321 (1923); Lewis, *ibid.*, **46**, 327 (1923). See Chapter XVI.

[2] Chapman and Jones, *J. Chem. Soc.*, **97**, 2463 (1910).

[3] Hinshelwood and Prichard, *J. Chem. Soc.*, **124**, 2730 (1923). Christiansen, *Z. physik. Chem.*, **103**, 99 (1922).

[4] Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921); Daniels, Wulf and Karrer, *ibid.*, **44**, 2402 (1922).

[5] Hinshelwood and Prichard, *J. Chem. Soc.*, **124**, 2725 (1923).

[6] Trautz and Bhandarkar, *Z. anorg. Chem.*, **97**, 2463 (1910).

[7] Hinshelwood and Topley, *J. Chem. Soc.*, **125**, 393 (1924).

reaction is supposed to take place in successive steps, each step being characterized by one of these active frequencies, so that if the density of any one of the frequencies is not increased, a great increase of the others would have no effect on the reaction velocity: besides being somewhat artificial this assumption is rendered very doubtful by Lewis' claim to have found a band in many reactions at a position calculated from the temperature coefficient. Lewis who also discusses this difficulty claims that since the solvent strongly absorbs infra-red radiation it acts as a protective screen for the solute so far as direct radiation is concerned; obviously, therefore, exposing such a solution in a fine spray to sunlight should greatly increase the reaction velocity but such an effect has not been observed.[1] Lewis also points out that in sunlight one is dealing with directed radiation and not temperature radiation:

"Since, however, the matter and radiation are in this case not at the same temperature, it is unjustifiable to compare the relative effects at all, for the following reasons. Owing to the lack of temperature equilibrium, when a substance is exposed to high temperature radiation, there is a tendency for the temperature of the matter to rise and that of the radiation to fall. This is brought about by absorption chiefly of a physical nature, that is, unaccompanied by chemical change probably at numerous positions, such absorption occurring in a layer of moderate thickness, so that throughout the bulk of the system the radiation density is scarcely altered from its original value prior to illumination, and, consequently, the rate is not appreciably affected."

This explanation can hardly be considered adequate in the light of the following considerations. The term temperature radiation is usually applied to black body radiation; for example, if we consider a closed space, the walls of which are at a uniform and constant temperature, the sum of the intensities of the radiation of all wave-lengths at the center of the space is a constant which depends only on the temperature of the walls. Temperature radiation is therefore the integral of the intensities of radiation of all wave-lengths emitted from a black body, a quantity which is proportional to the fourth power of the absolute temperature (Stefan-Bolzmann Law). We cannot speak of the temperature of a monochromatic ray for it is completely defined by its wave-length and its intensity and neither of these quantities contains the concept of temperature; monochromatic radiation coming from the sun is exactly the same as radiation of the same wave-length from a lamp bulb if the intensities are the same; consequently it is very difficult to see how a molecule absorbing radiation in a certain section of the spectrum can tell whether the radiation is temperature radiation or directed radiation. Lindemann [2] made an interesting suggestion intended to meet this difficulty by pointing out that a molecule may not dissociate immediately on attaining the critical increment; the rupture of the molecule may be produced a long time after the internal energy has attained the critical value. A further discussion of the difficulty is given by Lewis and McKeown.[3]

[1] T. W. J. Taylor, *Nature*, **108**, 210 (1921). See also Lewis, *ibid.*, **108**, 241 (1921).
[2] *Trans. Farad. Soc.*, **17**, 599 (1922).
[3] *J. Am. Chem. Soc.*, **43**, 1303 (1921).

Langmuir [1] criticized the radiation hypothesis on the basis that the similarity in form between the Arrhenius formula and Wien's law, which expresses the relation between the intensity of monochromatic radiation from a black body and the temperature of the body, is accidental; he pointed out that a number of properties which can scarcely be attributed to radiation follow a similar law.

A recent paper [2] dealing with some objections to the radiation theory contains the following:

"The main justification for regarding radiation as the origin and cause of physical and chemical change . . . lies in the fact that no other idea presents itself of sufficient generality to account for spontaneous or unimolecular processes, as well as multimolecular processes. Whatever criticisms therefore may be urged of attemps to apply the concept to thermal reactions must concern themselves with the mode of application, and not with the concept itself."

Other Hypotheses: Skrabal [3] has deduced a relation between the temperature coefficient of a reaction and the heats of formation of the various complexes present in the solution; he also gives a number of empirical rules regarding the relation of the temperature coefficient to the nature and constitution of the reacting substances, the medium and catalytic agencies. He claims that the change in the reaction velocity produced by alteration in any of these variables diminishes as the velocity increases; reaction of small velocity should therefore have a high temperature coefficient. He also claims that the higher the order of a reaction the greater is the temperature coefficient. He has applied these ideas in the study of the reaction between the iodide ion and the iodate ion, and also the reaction between iodine and the hydroxyl ion; these reactions are exceedingly complicated and the widest variations of the temperature coefficient were observed, depending on the conditions of the experiment: in some cases a negative temperature coefficient was obtained.[5] The complexity of the reaction between iodine and the hydroxyl ion may be judged by the statement [6] that when the reaction occurs in a solution of sodium carbonate and hydrogen carbonate, under certain conditions a reaction occurs the temperature coefficient k_T/k_{T+10} of which is 23 and the reaction is of the 13th order.

In a recent paper [7] a modification of the Arrhenius hypothesis was proposed to explain the high temperature coefficient of chemical reactions; considering the hydrolysis of cane sugar, Arrhenius suggested that the cane sugar was present in two forms and in this way accounted for the high temperature

[1] *Trans. Farad. Soc.*, **17**, 600 (1922).

[2] Lewis and McKeown, *J. Am. Chem. Soc.*, **43**, 1288 (1921).

[3] *Chem. Ztg.*, **37**, 1169 (1913); *Monatsh.*, **35**, 1157 (1914); **37**, 495 (1916).

[4] See however von Halban (*Z. physik. Chem.*, **67**, 129 (1909)), who concludes that a true unimolecular reaction possesses a higher temperature coefficient than a multi-molecular reaction. Dhar (*Z. anorg. Chem.*, **128**, 218 (1923)) gives a summary in which it is claimed that the temperature coefficient diminishes as the order and complexity of a reaction increases. Lewis (*J. Chem. Soc.*, **111**, 465, 469 (1917)) also discusses this problem.

[5] Skrabal and Weberitsch, *Ber.*, **47**, 117 (1914).

[6] Skrabal, *Monatsh.*, **32**, 815 (1911).

[7] Rice, *J. Am. Chem. Soc.*, **45**, 2808 (1923).

coefficient of the reaction. It has been already pointed out however that there is no *a priori* reason for supposing that the cane sugar exists in two forms; we might select any one of the three entities, cane sugar, water and hydrogen ion, taking part in the reaction, and by saying that it was present in two forms, we could deduce the Arrhenius equation; the justification for the particular selection would of course depend on the further development of the theory. In the proposed modification it is assumed that the hydrogen ion exists in two forms, active and inactive, in mass-action equilibrium. The active form which is present in very small concentration is identified as the unhydrated hydrogen ion, the hydrated form and the undissociated acid being assumed to have no catalytic activity; similar assumptions are made for hydroxyl-ion catalysis. "Whereas on both the Arrhenius theory and the radiation theory every chemical reaction should have a unique temperature coefficient depending on the heat of activation of the substance undergoing change, it is evident that this new theory predicts that chemical reactions will fall into comparatively few classes each having a characteristic temperature coefficient." Some support is obtained for this view from empirical observations in the laboratory which show that there is some tendency for reactions to fall into classes; for example a great many studies have been made of the acid hydrolysis of substances containing the carbonyl group, and almost without exception the value of k_{35}/k_{25} lies between 2.2 and 2.5. When we have a reaction in aqueous solution catalyzed by a strong acid in which the solvent does not enter directly into the reaction, the following argument is used:

"Assuming that the strong acid is practically entirely dissociated, the total hydrogen ion will be present as hydrated hydrogen ion and a minute quantity as unhydrated hydrogen ion; in this case the unhydrated hydrogen ion is supposed to be the only active molecule so that all these reactions should have the same temperature coefficient. This would hold for any solution in which the hydrogen ion is combined only with water, for the variation with temperature of the concentration of the unhydrated ion depends on its heat of combination. Therefore the temperature coefficient should not be affected by the presence of non-electrolytes or neutral salts since the affinity of hydrogen ion for water is so great [1] that it is unlikely that there will be any extensive combination between the hydrogen ion and these substances. . . . When, however, weaker acids were used as catalysts, that is, when the state of combination of the hydrogen ion was affected, the temperature coefficient fell." When the solvent enters directly into the reaction, the following argument is used: "In reactions which are hydrolytic in character I assume that there is a compound formed between the substance A undergoing hydrolysis and the water; that, in general, only a small fraction of the substance A is present as hydrate, and that the hydrolysis takes place by collision of the unhydrated hydrogen ion with the hydrate. It will be seen that the hydrate of the substance A now becomes an active molecule and the temperature coefficient of the reaction will depend on whether the heat of hydration of A is positive or negative. Practically all cases of hydrogen ion catalysis are thus covered and the treatment of hydroxyl ion catalysis is exactly similar."

The whole basis of this reasoning is the assumption that the mass action law in its classical form is true, and that its apparent failure is due to using stoichiometric equations which do not represent even approximately the

[1] Born, *Ber. physik. Ges.*, **21**, 679 (1919); Fajans, *ibid.*, **21**, 549 (1919). A resumé of this work is given by Taylor, Newer Aspects of Ionization Problems. *Trans. Amer. Electrochem. Soc.*, **43**, Preprint (1923).

reactions taking place in the solution; when these stoichiometric equations are replaced by equations which are supposed to represent more nearly the reactions actually occurring in the solution, it is shown that certain molecules are connected with an equilibrium constant in such a way that their concentrations vary rapidly with the temperature. These are referred to as active molecules, and it is due to these that "slow" reactions have a high temperature coefficient. "The temperature coefficient of a reaction is fixed by the number and nature of these active molecules, and all types of reaction which have the same active molecules will have exactly the same temperature coefficient. The variation with temperature of the concentration of the active molecule will depend on its heat of combination with the solvent or other constituents of the solution with which it combines. According as this heat of combination is positive or negative the concentration of the active molecule will increase or decrease with rise of temperature; an active molecule therefore on this theory has no particular virtue because of its internal energy content. If we measure the velocity of a reaction at two temperatures, and substitute the values in the Arrhenius formula, we shall obtain directly the heat of combination of the active molecule if its formation is represented by an equation such as $B + C \rightleftarrows A$, where A is the active molecule. In other cases the calculated value of Q will usually be a simple multiple or sub-multiple of the heat of reaction, and in cases where there are more than one active molecule the value of Q will be the algebraic sum of these quantities. Since Q is a heat of reaction, it will vary slightly with the temperature, and this variation could be calculated if the specific heats of the reactants and resultants were known as functions of the temperature. In those reactions which have the same active molecules, the value of Q and its variation with the temperature will be the same.

This discussion of the various hypotheses which have been advanced to explain the high temperature coefficient of reaction velocity points, perhaps, to the desirability of having more data available on the temperature coefficients of chemical reactions, especially simple reactions not complicated by secondary reactions occurring at the same time. Hundreds of investigations have been made on sugar inversion and other hydrolytic reactions which are probably consecutive reactions and into which the solvent enters directly; in such cases the necessity for making several questionable assumptions regarding the mechanism of the reaction seriously diminishes the value of the results for testing one or other of these hypotheses.

Catalysis

It has been stated at the beginning of this chapter that practically all reactions that proceed with measurable speed are catalytic in character; consequently it is necessary to consider the nature and mode of action of catalysts. Since Ostwald[1] introduced his criterion of a catalyst as something which increases the rate of a chemical reaction without modifying the energy factors,

[1] *Z. physik. Chem.*, **15**, 705 (1894).

it has been customary to regard reactions as taking place at a relatively slow rate in absence of a catalyst, its only function being to increase the rate of a change which is already taking place. Ostwald regards the catalyst as a completely foreign substance and the energy used up in adding it to the system is regained by its removal, or vice-versa; he denies the supposition of Berzelius [1] that there is a special catalytic force and asserts that catalytic action is simply the hastening of a natural transformation towards equilibrium with the consequent reduction of the free energy of the system. Various popular illustrations of this have been given such as the comparison of a catalyst to a lubricant which diminishes friction in a machine or to a whip which makes a horse go faster. There is however another point of view, namely, that the catalyst is essential and without the catalyst the reaction would not take place. On the Ostwald view we are tempted to regard the catalyst as comparable with the crowd which cheers the players in a game, whereas on the second view we must regard the catalyst as an essential player, perhaps the captain of the team who directs the plays and without whom the game could not take place. Arrhenius [2] originally put forward the view that chemical action is necessarily preceded by a process of molecular activation; in spite of many diverse views as to the mechanism of molecular activation, the idea has received extensive support and forms the basis of several explanations of the high temperature coefficient of chemical reactions; most authors are agreed that the activation is an absorption of energy by the molecule, so that the activated form has more energy than the non-reactive form. As pointed out by Norrish,[3] there is one fact that has not received very much consideration, namely, that even the most reactive substances become inert on complete desiccation, but regain their lost activity by the addition of a trace of some polar substance. With very few exceptions this loss of reactivity on desiccation is a general rule of chemical reactivity and would appear to necessitate a revision of our views of activation; the resting form of a molecule must be a far more inert substance than hitherto supposed, and apparently requires the association of some polar molecule before activation can take place. Since the main characteristic of a polar molecule is its strong unbalanced field of force, it is probable that its function as a catalyst is to weaken, by close association, the intramolecular forces of the resting molecule and render it more easily disintegrable. Norrish believes that these considerations coupled with the kinetic theory could form the basis for a complete explanation of all the phenomena of chemical reactivity. Molecular activation is regarded as a change of configuration or distortion of the molecule brought about by close association with a polar catalyst; since the molecule is removed from its stable state, such a change of configuration must take place with the absorption of energy and thus the activated molecule will be in a more highly energized state than the resting molecules. Experiments on the combination of bromine and ethylene support these views; when dry, these two substances

[1] *Ann. chim. phys.*, **61**, 146 (1836).
[2] *Z. physik. Chem.*, **4**, 226 (1889); **28**, 317 (1899).
[3] *J. Chem. Soc.*, **124**, 3006 (1923).

do not react [1] in the gaseous phase at 0° C. but only on the glass walls of the container. Norrish showed that when the glass walls are covered with a layer of paraffin wax the reaction practically ceases; if, however, a polar substance like stearic acid is substituted for the non-polar paraffin wax, the reaction proceeds even more quickly than when the glass walls are bare.

The work of Lowry [2] also indicates that activation by a suitable catalyst is necessary for a reaction to proceed; a study of the isomeric change of nitrocamphor in a number of carefully purified solvents showed that the velocities observed are not characteristic of the particular solvent but are due to minute traces of alkaline impurities which are still present even after the most rigorous purification. When all traces of aminic impurities are removed, and when the solution is kept in a silica flask to prevent contamination by alkali from the glass, the velocity of isomeric change is practically zero. Similar conclusions may be drawn from the experiments of Meyer and his co-workers on aceto-acetic ester [3]; the remarkable ease with which the forms change to the equilibrium mixture is shown to be a catalytic phenomenon which does not take place in absence of the hydroxyl ion; thus, in the vapor state the two forms are stable and do not undergo isomeric change; it is only when one of the isomers is in contact with glass or when there is some other source of hydroxyl ions present that the isomer changes to the equilibrium mixture; similar results are obtained for other keto-enol isomers. It must be admitted however that the question is far from being settled, since a commonly accepted criteria of catalytic action is that a catalyst is incapable of starting a reaction and can only modify the velocity of a reaction already taking place. The foregoing discussion has been given to justify the viewpoint adopted in this section that activation by a catalyst is necessary for a reaction to proceed. Rideal and Taylor [4] point out the difficulty of making an experimental test: "The analytical detection of an extraordinarily slow process in the absence of an unlimited time factor is a matter of extreme difficulty; secondly, in view of the universality of catalytic action it would be difficult to devise an experimental test in which *all* catalytic agencies were excluded, since, as is frequently the case, even the walls of a containing vessel may exert a considerable catalytic influence."

In a recent discussion of catalytic criteria based on the radiation hypothesis Lewis [5] emphasizes an important point; if we ascribe a definite stoichiometric molecular mechanism to the action of the catalyst, then it may be said to render a reaction possible by supplying the necessary matter; otherwise it merely accelerates a reaction already proceeding by increasing the radiation density of that region in which the substrat absorbs; since the ordinary thermal radiation present contains all wave-lengths or frequencies, a reaction which does not require compound formation with the catalyst would proceed slowly even in complete absence of a catalyst.

[1] Stewart and Edlund, *J. Am. Chem. Soc.*, **45**, 1014 (1923).

[2] *J. Chem. Soc.*, **75**, 211 (1899); Lowry and Magson, *ibid.*, **93**, 107, 119 (1908).

[3] Meyer and Schoeller, *Ber.*, **53**, 1410 (1920); Meyer and Hopff, *ibid.*, **54**, 579 (1921).

[4] Catalysis in Theory and Practice, p. 27. Macmillan, 1919.

[5] *J. Chem. Soc.*, **115**, 1360 (1919).

The criteria which have been suggested as characteristic of catalytic reactions in general are the following: [1]

(1) The chemical composition of a catalytic agent is unchanged on completion of the reaction process; hence minimal amounts of a catalytic agent are adequate for the transformation of large quantities of reacting substances.

(2) A catalyst modifies the velocities of two inverse reactions to the same degree and therefore cannot affect the final state of equilibrium.

(3) A catalytic agent is incapable of starting a reaction; it can only modify the velocity of a reaction already taking place.

The application of these criteria to catalysis in homogeneous systems may now be considered. Criterion (1) does not seem to be very satisfactory when considered in relation to homogeneous systems; for, consider the addition of hydrochloric acid gas at concentration c_1 to an aqueous solution of cane sugar, the transformation of the cane sugar to a mixture of fructose and glucose and then the removal of the hydrochloric acid to its original gaseous condition at concentration c_1; it hardly seems possible that the free energy change when the hydrochloric acid goes into solution is equal and opposite to the free energy change when it is removed from the solution at equilibrium and that this is a general rule for all reactions; consequently in homogeneous reactions we cannot say that the catalyst is unchanged on completion of the reaction. Indeed, if we adopt the double compound theory of catalytic action and apply it to the hydrolysis of methyl acetate in aqueous solution by hydrochloric acid, at the beginning of the reaction the catalyst is partly in combination with the methyl acetate but at the end of the reaction is partly in combination with acetic acid and methyl alcohol. We can get over this difficulty by considering the reactants and resultants and the catalyst contained in a van't Hoff equilibrium box, the whole system being of course at equilibrium; now if we conduct the reaction reversibly by adding the reactants at their equilibrium concentrations and simultaneously withdrawing the resultants at their equilibrium concentrations, we leave the catalyst unchanged and this process can be conducted indefinitely. If we change the concentration of the catalyst in the equilibrium box, there is no thermodynamic reason for assuming that the equilibrium point of the reaction is unchanged; however, by postulating that the catalyst is present in very dilute solution, we may apply the mass action law and assume that the rates of the opposed reactions are altered in the same ratio, leaving the equilibrium point unchanged. Therefore, when postulating the criteria for catalysis in homogeneous systems, we may omit criterion (3) and make only the following two statements:

(*a*) In a system at equilibrium a catalyst can bring about the transformation of reactants into resultants indefinitely without being itself changed in the process.

(*b*) In systems containing only small amounts of a catalyst, it modifies the velocities of the two inverse reactions to the same degree; consequently the equilibrium point in such systems is independent of the concentration of the catalyst.

[1] Compare Rideal and Taylor, *ibid.*, Chap. 2.

In a discussion [1] of criterion (2) on the basis of the radiation hypothesis, the conclusion is reached that this is not true in general; in homogeneous systems it approximates more closely to experiment the smaller the heat effect accompanying a reaction.

Hydrogen Ion and Hydroxyl Ion Catalysis: Since the great majority of reactions in homogeneous systems are catalyzed by these ions, it seems well to discuss catalysis with reference to such reactions. The fact that the catalytic activity of acids in aqueous solution is approximately proportional to the degree of dissociation as determined by electrolytic measurements led to the identification of the hydrogen ion as the active catalyst; indeed the well-known experiments of Arrhenius [2] on the inversion of sucrose by weak acids in presence of the corresponding salt gave results which furnished the most convincing evidence in favor of the view that, apart from a small neutral salt effect, the catalytic activity of an acid is determined by the concentration of the hydrogen ion in the acid solution; the simple hydrogen ion theory of acid catalysis rests very largely on the evidence afforded by these measurements. About this same time it was found [3] that the rate of inversion of sucrose by weak acids was greatly augmented by the addition of the neutral salts of strong acids; for example, the presence of 0.125 N potassium chloride increases the catalytic activity of 0.025 N acetic acid by about 12 per cent. Arrhenius therefore proposed a modification of his dissociation theory by postulating that dissolved salts increase the dissociation constants of weak acids present in solution; presumably the water acquires a greater dissociating power or the salt itself acts as a dissociating medium. This view was generally accepted for about twenty years. During this time however results were accumulating which indicated that the undissociated molecule of the catalyzing acid might be catalytically active, and that there was a general relationship between the catalytic power of the undissociated acid and its dissociation constant; since the undissociated molecule in the case of strong acids appeared to be more active than the hydrogen ions, it soon became obvious that these results might explain the anomalous neutral salt action observed by Arrhenius without adopting the hypothesis that the dissociating power of the medium was altered.

The view that the catalytic effect represents the result of two simultaneous changes in which the active agents are the hydrogen ion and the non-ionized acid was developed by a number of workers [4] and became known as the dual theory of acid catalysis. The work of Goldschmidt on ester formation in

[1] Lewis, *J. Chem. Soc.*, **115**, 1362 (1919).

[2] *Z. physik. Chem.*, **5**, 1 (1890).

[3] Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899).

[4] Senter, *J. Chem. Soc.*, **91**, 460 (1907); Lapworth, *ibid.*, **93**, 2197 (1908); Snethlage, *Z. Elektrochem.*, **18**, 539 (1912); Acree, *Am. Chem. J.*, 1907 to 1913; Goldschmidt, *Z. physik. Chem.*, **70**, 627 (1910); *idem*, *ibid.*, **81**, 30 (1912); Bredig, *Z. Elektrochem.*, **18**, 535 (1912); Taylor, *Medd. K. Vetensk. Nobelinst.*, **2**, 35, 37 (1913); Dawson and Powis, *J. Chem. Soc.*, **103**, 2135 (1913); Ramstedt, *Medd. K. Vetensk. Nobelinst.*, **3**, 1 (1915); Taylor, *J. Am. Chem. Soc.*, **37**, 551 (1915); Lapworth, *J. Chem. Soc.*, **107**, 857 (1915); Dawson and Reiman, *J. Chem. Soc.*, **107**, 1426 (1915).

methyl and ethyl alcohols led to the conclusion that both the hydrogen ions and the non-ionized acid are catalytically active since, when sufficient salt of the catalyzing acid is added to reduce the ionization of the latter practically to zero, the reaction still proceeds at a definite rate; the assumption is made that this is due to a complex of the non-ionized portion of the acid with the reactant. Snethlage showed that his observations on reactions catalyzed by acids in ethyl alcohol solutions could be explained on the basis of this theory; he calculated values for the ratio between the catalytic activity of the undissociated acid and that of an equal concentration of hydrogen ion, and showed that the greater the strength of the acid the greater is the catalytic activity, k_M, of the non-ionized portion as compared with the catalytic activity, k_H, of the hydrogen ion; for weak acids the ratio k_M/k_H is a very small fraction; but for acids like hydrochloric acid the ratio is greater than 1. The fact that the rate of hydrolysis increases more rapidly than the concentration of the hydrochloric acid is accounted for on the assumption that in aqueous solution the catalytic activity of the non-ionized acid is about double that of hydrogen ions in equivalent concentration; similarly the accelerating effect of neutral salts is attributed to their effect in increasing the concentration of the non-ionized portion of the acid.

Later developments of this theory [1] postulate that the number of catalytically active particles is much greater than is ordinarily supposed; instead of considering the simple equilibrium equation $HCl \rightleftharpoons H^+ + Cl^-$ in connection with the hydrolysis of, for example, methyl acetate by hydrochloric acid, we should realize that this simple equation represents very incompletely the reactions occurring; really there is a complex series of equilibria between many different molecular and ionic types so that we have present as well as the simple hydrogen ion H^+, such compounds as $(H.H_2O)^+$, $(H.CH_3COOCH_3)^+$, $(HCl.H_2O)$, $(H.CH_3COOH)^+$, etc. If we ascribe a catalytic activity to the undissociated molecule, it is only logical to take these other compounds into consideration also; the problem thus becomes very difficult, for we have at present no idea of their relative catalytic activities and no method of measuring even their relative concentrations.

The whole problem may, however, be put on a much simpler basis by considering the possibility that the simple hydrogen ion may have properties not possessed by compounds containing it; for example, when the simple hydrogen ion combines with ammonia, the resulting ammonium radical $(H.NH_3)^+$ has no catalytic activity and it is quite reasonable to assume that the similar compound $(H.H_2O)^+$ has no catalytic activity; indeed, when we consider that the reaction

$$H^+_{gas+} + nH_2O = (H.nH_2O)^+$$

evolves 262,000 cal. per mole,[2] it seems quite unreasonable to ascribe a similarity in catalytic powers to the two substances H^+ and $(H.nH_2O)^+$. Lapworth [3]

[1] See Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921).

[2] Fajans, *Ber. phys. Ges.*, **21**, 709 (1919).

[3] Fitzgerald and Lapworth, *J. Chem. Soc.*, **93**, 2163 (1908); Lapworth, *ibid.*, **93**, 2187 (1908).

and his co-workers first put forward the view that the hydrated hydrogen ion has little or no catalytic activity; they examined the following widely different examples of hydrogen ion catalysis in organic solvents, and showed that small quantities of water produce a marked retardation in all cases; the decomposition of diazoacetic ester, the esterification of carboxylic acids, the change of hydrazobenzene into benzidine and the bromination of ketones. Those reactions which occurred in both water and alcohol were found to go enormously faster in alcohol, and minute quantities of water in the alcohol produced a great retardation of the velocity. Lapworth accounts for this by supposing that the water causes a reduction in the number of non-hydrated hydrogen ions, which he supposes to be the active catalytic agent. He concludes: "The proposition that free hydrogen ions are responsible for the catalytic activity of acids leads to the conclusion that they must be relatively few in number in aqueous solution. On the other hand, the original conception of hydrogen ions was applied to explain the conductivity of acids in aqueous solution, so that the terms are not synonymous. In the latter case, they must be complex ions, probably of the form $(H_2O.H)^+$." Dawson,[1] from experiments on the reaction between acetone and iodine in water and water-alcohol mixtures, also supported this view; 0.5 per cent of water reduced the rate to one fifth and 1 per cent of water reduced the rate to one tenth of its value in pure alcohol; further, in alcohol solutions containing small quantities of water, the reaction velocity is proportional to the concentration of the acetone, but is not proportional to the concentration of the acid catalyst; in such solutions the velocity increases much more rapidly than the concentration of the acid catalyst. For example, in an alcoholic solution containing one half per cent of water, an increase of the concentration of the sulfuric acid catalyst from 0.03 *M* to 0.15 *M* increases the velocity nearly ten times. He concludes:

"By comparison of the observations in aqueous with those in alcoholic solution, we are led to the conclusion that the ionic component responsible for the catalytic effect is the free hydrogen ion, and that the effect of the hydrated ion is relatively unimportant. The concentration of the free hydrogen ions is very small in comparison with the total ion concentration, and, in order to produce the observed effects, it must be assumed that their specific catalytic activity is very great. Since the ratio of the free hydrogen ion to the total hydrogen ion concentration is so small, the electrical conductivity of the solution is mainly determined by the complex ions, and the catalytically active ions are of little consequence in so far as the conductivity of the acid solution is concerned."

The surprising variations obtained in hydrogen ion catalysis by changing the solvent and the catalyzing acid are illustrated by some results obtained by Dawson and Powis:[2] in an alcoholic solution of hydrochloric acid the reaction between acetone and iodine is approximately one thousand times as fast as in an aqueous solution of hydrochloric acid of the same concentration; in aqueous solution the reaction proceeds at the same rate when catalyzed by equal concentrations of hydrochloric acid and trichloracetic acid, but in alcohol hydrochloric acid is 200 times as active catalytically as trichloracetic acid. Mono-

[1] *J. Chem. Soc.*, **99**, 1 (1911); Dawson and Powis, *ibid.*, **105**, 1093 (1914).
[2] *Ibid.*, **103**, 2135 (1913).

chloracetic acid and dichloracetic acid which are moderately strong acids in water have practically no catalytic activity in alcohol.

The view that only the unhydrated hydrogen ion is catalytically active has many advantages and it appears probable that further development of this view will permit of a quantitative explanation of all the abnormalities in the catalytic activity of acids; this has already been done by Lapworth for the effect of small quantities of water on hydrogen ion catalysis in alcohol solution, and the treatment is quite as satisfactory as that of Goldschmidt,[1] who assumes that the active catalytic agent of the esterification process is an alcoholate $(C_2H_5OH.H)^+$; this reacts with the acid present to give the ethyl ester. On Goldschmidt's view, the water diminishes the rate of the reaction by formation of the hydrogen ion hydrate, since he regards both this and the free hydrogen ions as being inactive catalytically. It is evident that the Goldschmidt view must be modified to meet every different reaction, whereas the Lapworth view does not require this modification. This discussion may be closed by a brief reference to neutral salt action; since the ions of these salts are heavily hydrated, it is evident that their addition to an aqueous solution will increase the concentration of free hydrogen ions and therefore increase the catalytic power of an acid; this gives a qualitative explanation of neutral salt action; further, the more highly hydrated an ion the greater should be its neutral salt action, which is in agreement with experiment. The fact that neutral salt action is independent of the substrat [2] supports the view that this effect is connected with the catalyst rather than with the substrat as suggested by Arrhenius and later by Euler.[3]

Catalysis by Metallic and Non-metallic Ions: The decomposition of hydrogen peroxide in aqueous solution is accelerated by the presence of iron salts [4] in the solution, and both the molecules of the ferric salt and the ferric ions appear to catalyze the reaction; the rate of evolution of oxygen in presence of a mixture of iron and copper salts is much more rapid than the rate which may be calculated on the assumption that each salt acts independently; a small amount of a copper salt greatly accelerates the decomposition of hydrogen peroxide by iron salts in acid solution, whereas other metallic salts do not appear to have this promoter effect. The decomposition of hydrogen peroxide by the bromide ion has been studied by Bray and Livingston [5] and the decomposition by the iodide ion has been studied by Walton [6] and by Harned.[7] The concentration of the iodide ion remains constant and all the peroxide oxygen is evolved; the velocity is proportional to the concentration of the

[1] *Z. Elektrochem.*, **12**, 432 (1906).

[2] Taylor, *Medd. K. Vetensk. Nobelinst.*, **2**, No. 34 (1913).

[3] *Z. physik. Chem.*, **4**, 226 (1889); *ibid.*, **32**, 348 (1900).

[4] von Bertalan, *Z. physik. Chem.*, **95**, 328 (1920); Duclaux, *Bull. soc. chim.*, **31**, 961 (1922); Mummery, *J. Soc. Chem. Ind.*, **32**, 889 (1913); Bohnson, *J. Phys. Chem.*, **25**, 19 (1921); Bohnson and Robertson, *J. Am. Chem. Soc.*, **45**, 2493, 2512 (1923).

[5] *J. Am. Chem. Soc.*, **45**, 1251, 2048 (1923).

[6] *Z. physik. Chem.*, **47**, 185 (1904).

[7] *J. Am. Chem. Soc.*, **40**, 1463 (1918).

hydrogen peroxide and to the concentration of the iodide ion. Walton represents the mechanism of the reaction in the following way:

$$H_2O_2 + I' = H_2O + IO', \quad (1)$$

$$H_2O_2 + IO' = H_2O + O_2 + I'. \quad (2)$$

(1) is a slow measurable reaction followed by (2) an extremely rapid reaction. Clayton [1] has shown that hydrogen peroxide is extremely sensitive to the presence of small quantities of impurities and only by observing many precautions can the velocity of decomposition of hydrogen peroxide in pure water be obtained. The possibility of the decomposition being also partly a wall reaction is discussed in the succeeding chapter (p. 963).

Slater [2] has studied the kinetics of the reaction between benzene and chlorine when catalyzed by ferric chloride, tin tetrachloride and iodine chloride; the reaction is remarkable in that the temperature coefficient with iodine chloride as catalyst is unusually low whereas with other catalysts the normal value is obtained.

The catalytic effect of mercury salts has been studied for a number of reactions; using mercuric nitrate as catalyst, oxalic acid in almost pure condition may be prepared [3] from acetylene and nitric acid; similarly, acetaldehyde may be prepared from acetylene and water by using mercuric sulfate in sulfuric acid solution; [4] benzene and its homologues may be converted into a variety of nitro derivatives directly by nitric acid under the catalytic influence of mercuric nitrate.[5] Mercuric sulfate is a most effective catalyst for the oxidation of naphthalene to phthalic acid,[6] and a mixture of mercuric sulfate with copper sulfate has a greater catalytic effect than would be expected from the single effects.[7]

Water as a Catalyst: Unless special precautions are taken, every chemical reaction takes place in presence of water; this is due largely to the presence of water vapor in the air and also on the surface of the glass vessels containing the reactants. If we exclude all traces of water from chemical reactions, the results obtained are very interesting and unexpected; thus, we find that sodium, even if heated to dull redness, will not combine with dry chlorine, and many other metals [8] such as magnesium, zinc and Dutch metal will remain untarnished over a period of months in the dry gas; introduction of a trace of moisture causes rapid action, in some cases with incandescence. Sodium or potassium may be distilled [9] in dry oxygen without action occurring; similar

[1] *Trans. Farad. Soc.*, 11, 164 (1915).
[2] *J. Chem. Soc.*, 83, 729 (1903).
[3] Kearns, Heiser and Nieuwland, *J. Am. Chem. Soc.*, 45, 795 (1923).
[4] Vogt and Nieuwland, *J. Am. Chem. Soc.*, 43, 2071 (1921).
[5] Davis, Worrell, Drake, Helmkamp and Young, *J. Am. Chem. Soc.*, 43, 594 (1921).
[6] Groebe, *Ber.*, 29, 2806 (1896).
[7] Bredig and Brown, *Z. physik. Chem.*, 46, 502 (1903).
[8] Wanklyn, *Chem. News*, 20, 271 (1869); Cowper, *J. Chem. Soc.*, 43, 153 (1883).
[9] Holt and Sims, *J. Chem. Soc.*, 65, 432 (1894).

results [1] are obtained with carbon, sulfur, boron and phosphorus but selenium, tellurium, arsenic and antimony react with equal readiness in moist or dry oxygen. In the experiment with carbon, Baker heated a rod of dry charcoal by passing a current through a coil of fine platinum wire surrounding the charcoal.

"The carbon did not catch fire, and the glow disappeared directly the current was stopped. With a stronger current, the platinum was heated nearly to whiteness; the carbon showed visible combustion for two seconds after which the glow died out. . . . A similar experiment was tried with a rod of carbon in moist oxygen. On raising the temperature to dull redness by means of the heated wire, the carbon caught fire, and, although the current was immediately broken, there was no cessation of the combustion until the rod was entirely consumed. Such combustion as did occur in dry oxygen produced mainly carbon monoxide."

Many similar examples of loss of reactivity have been observed, such as the non-reactivity [2] of dry hydrochloric acid with sodium, aluminium, silver nitrate and Iceland spar; also, the non-reactivity of dry hydrogen sulfide [3] with many oxides and salts which react with great rapidity when moist. In connection with homogeneous catalysis the subject was first brought prominently into notice by Dixon [4] who, in the course of some experiments on mixtures of carbon monoxide and hydrogen with insufficient oxygen to burn them completely, found that dry carbon monoxide and dry oxygen do not combine when sparked; he found that drying with phosphorous pentoxide for only one hour makes the gases moderately non-reactive, and the greater the degree of dryness reached the more inert are the gases; traces of hydrogen, pentane, hydrogen sulfide or hydrogen chloride make the carbon monoxide-oxygen mixture inflammable even if the substance added is quite dry.

We have now a large number of examples of loss of reactivity when all traces of moisture are removed from substances which ordinarily react readily; Baker [5] has shown that hydrogen and oxygen when dry do not combine, even at a temperature of about 1000° C., obtained by melting a coil of silver in the gaseous mixture; a platinum wire, however, just on reaching visible redness causes an explosion of the dried gases. The reaction is a very sensitive one; the gases must be very pure, and the containing vessel must be of hard glass and must be very carefully cleaned and dried. Ammonia and hydrochloric acid do not react [6] when dry; a trace of water, however, causes dense white fumes and rapid contraction; Kahlenberg [7] has shown that if dry ammonia is passed into a dry solution of hydrochloric acid in benzene, reaction occurs; moreover, the benzene vapors are sufficient to cause the reaction to occur.

[1] Baker, *Phil. Trans.*, **79A**, 583 (1888).

[2] Cohen, *Chem. News*, **54**, 305 (1886); Hughes and Wilson, *Phil. Mag.*, **34**, 117 (1892); Hughes, *ibid.*, **35**, 531 (1893).

[3] Hughes, *Phil. Mag.*, **33**, 471 (1892).

[4] *Phil. Trans.*, **175A**, 617 (1884).

[5] *J. Chem. Soc.*, **81**, 400 (1902).

[6] Helmholtz and Richards, *Ann. Phys. Chem.*, **40**, 161 (1890); Hughes, *Phil. Mag.*, **35**, 531 (1893); Baker, *J. Chem. Soc.*, **65**, 611 (1894).

[7] *J. Phys. Chem.*, **6**, 13 (1902).

Other pairs of gases which do not combine when dry are: nitric oxide and oxygen,[1] cyanogen and oxygen,[2] hydrogen and chlorine,[3] and ammonia and carbon dioxide.[4] There are a number of substances which, when moist and in the vapor state, are largely dissociated but do not dissociate when dry: Baker showed [5] that this occurs with ammonium chloride, nitrogen peroxide (N_2O_4), nitrogen trioxide (N_2O_3), mercurous chloride (Hg_2Cl_2) [6] and phosphorous pentachloride. Finally there are the remarkable experiments of Baker [7] in which he showed that a number of common liquids when dried over a period of years boil at temperatures from 14 to 60 degrees C. higher than the undried liquids.

The commonly accepted explanation of these phenomena is that the water acts as a catalyst and brings the different molecular species to equilibrium; a mixture of ammonium chloride, ammonia and hydrochloric acid without water present would be similar to a mixture of sulfur trioxide, sulfur dioxide and oxygen without a platinum or other catalyst present; in either case, changing the conditions does not alter the relative proportions of the substances even though the concentrations are far removed from equilibrium. Dixon [8] suggested a mechanism for the oxidation of carbon monoxide based on the intermediate compound theory of catalysis.

"Since it has already been shown that carbonic oxide is oxidized by steam at a high temperature, it seemed possible that carbonic oxide is incapable of direct union with oxygen, but is burnt indirectly by steam with liberation of hydrogen. The steam would act as a carrier of oxygen to the carbonic oxide by a process of alternate oxidation and reduction somewhat analogous to that undergone by nitric oxide in the sulfuric acid chamber."

Traube [9] suggested an alternative mechanism for the catalytic action of the water by postulating the formation of hydrogen peroxide, the water vapor simply acting as a carrier for the oxygen. Smits[10] has recently put forward the view that the inactivation of substances by intensive drying is due to the existence of two types of molecules, the drying process causing a shift of the equilibrium between these two types in the direction of formation of the inactive molecules. He applies this explanation when discussing the observation[11] that moist ammonium chloride is almost completely dissociated but when dry is not appreciably dissociated in the gaseous condition. G. N.

[1] Baker, *loc. cit.*

[2] Dixon, *J. Chem. Soc.*, **49**, 384 (1886).

[3] Pringsheim, *Ann. Phys. Chem.*, **32**, 384 (1887); Dixon and Harker, *Man. Lit. Phil. Soc.*, **3**, 118 (1889); *idem*, *ibid.*, **4**, 1 (1890); Baker, *J. Chem. Soc.*, **65**, 611 (1894); Mellor and Russel, *ibid.*, **81**, 1272 (1902).

[4] Hughes and Soddy, *Chem. News*, **69**, 138 (1894).

[5] *J. Chem. Soc.*, **65**, 611 (1894); *ibid.*, **77**, 646 (1900); *ibid.*, **91**, 1862 (1907).

[6] See also Smith and Menzies, *Z. physik. Chem.*, **76**, 713 (1911).

[7] *J. Chem. Soc.*, **121**, 568 (1922).

[8] *Phil. Trans.*, **175A**, 617 (1884).

[9] *Ber.*, **26**, 1471 (1893).

[10] *Proc. Acad. Sci. Amsterdam*, **26**, No. 3 (1923).

[11] *Rec. trav. chim.*, **42**, 826 (1923).

Lewis [1] has criticized this view and supports the more rational view that the trace of water acts as a catalyst; he points out that ammonia, a substance very similar to water, acts as a catalyst for the interconversion of the two forms of sulfur, S_λ and S_μ, and in absence of ammonia the two forms remain in their initial state without reaching equilibrium even under extreme change of condition.

The hypothesis that water is a catalyst in these reactions cannot, however, be a complete explanation of the facts; Baker [2] has pointed out that the water formed by the combination of hydrogen and oxygen will not catalyze the reaction between the gases; further, there is the remarkable experiment [3] in which dried benzene with a boiling point of 106° C. can be poured on to water and the water boiled through it without the benzene undergoing change; it is not until the benzene is in contact with the water for several days that it regains its original boiling point of 80° C. These experiments suggest either that Smit's view is correct or that the water is not the actual catalyst; possibly the water partly combines with the reactants or with the walls of the vessel to produce the actual catalyst.

Negative Catalysis: A number of reactions have been studied which are sensitive to the presence of foreign substances in such a way that the velocity is sometimes increased and sometimes diminished; thus, Bigelow [4] found that the rate of oxidation of aqueous sodium sulfite by atmospheric oxygen is greatly affected by the presence of organic compounds; the results for the different compounds are very erratic, for example, oxalic acid and tertiary butyl alcohol have no effect, propyl alcohol and acetone have a marked effect and benzyl alcohol has an enormous effect; most aromatic compounds reduce the velocity greatly. Similar results were obtained by Young [5] who studied the rate of oxidation of stannous chloride by atmospheric oxygen; in this reaction, hydrogen sulfide is such a powerful catalyst that its presence at a concentration of 0.000005 N increases the velocity of the reaction about 25 per cent; on the other hand, salts of manganese and chromium, various alkaloids, mannite, aniline and potassium cyanide greatly reduce the velocity. Young [6] also studied the rate of oxidation of aqueous sodium sulfite and found many astonishing examples of inhibition; in alkaline solution, 0.000005 M brucine hydrochloride reduces the velocity to one hundredth of the normal rate and its effect can still be detected at concentrations about 0.0000001 M; similar effects though not quite so great are obtained with other alkaloids, with cane sugar and with ammonium chloride. Young concludes from his own and Bigelow's results that this inhibiting effect is shown in some degree by all organic compounds. Titoff [7] has a comprehensive memoir on negative

[1] *J. Am. Chem. Soc.*, **45**, 2836 (1923).
[2] *J. Chem. Soc.*, **81**, 400 (1902).
[3] Baker, *J. Chem. Soc.*, **121**, 568 (1922).
[4] *Z. physik. Chem.*, **26**, 493 (1898).
[5] *J. Am. Chem. Soc.*, **23**, 119, 450 (1901).
[6] *J. Am. Chem. Soc.*, **24**, 297 (1902).
[7] *Z. physik. Chem.*, **45**, 641 (1903).

catalysis in homogeneous systems in which he made a further study of the oxidation of aqueous sodium sulfite; the rate of oxidation is very slow in absence of added catalyst; it is a reaction of the first order, the rate being proportional to the concentration of the sodium sulfite but independent of the concentration of oxygen. Many salts of heavy metals accelerate the reaction, notably copper sulfate, which even at 0.0000000000001 N produces a measurable acceleration. Mannitol and stannic chloride diminish the rate of oxidation, and from experiments on the simultaneous effect of the positive catalyst (copper sulfate) and a negative catalyst (mannitol or stannic chloride) he supports the view that a negative catalyst diminishes the velocity by suppressing the activity of a positive catalyst.

Senter [1] has shown that nitric acid is a negative catalyst in the reaction between silver nitrate and halogen aliphatic acids in alcoholic solution; for brom-acetic acid the following equation represents the change:

$$CH_2Br.COOH + AgNO_3 + 2C_2H_5OH = CH_2(OC_2H_5)COOH + AgBr + C_2H_5NO_3.$$

This is accompanied by another change,

$$CH_2Br.COOAg + C_2H_5OH = CH_2(OC_2H_5)COOH + AgBr,$$

since an equilibrium must be established according to the following equation:

$$CH_2Br.COOH + AgNO_3 \rightleftharpoons CH_2BrCOOAg + HNO_3.$$

The change is further complicated by the fact that the silver bromide formed is catalytically active, so that the mechanism of the negative catalytic effect is still somewhat uncertain. Senter has also shown that, when halogen-substituted acids are hydrolyzed, both the undissociated acid molecule and the acid anion undergo hydrolysis; retardation by the halogen acid formed occurs when the rate of hydrolysis of the ion is faster than that of the undissociated acid molecule. Evidently the retardation is due to an increase of the less active undissociated acid molecule at the expense of the more active anion.

The mathematical representation of negative autocatalysis given by Ostwald [2] is

$$\frac{dx}{dt} = k_1(a - x) - k_2x(a - x),$$

where the symbols have their usual significance, x being the concentration of negative catalyst formed after time t; possibly because of complicating simultaneous reactions this does not represent experimental results and an empirical equation [3] of the form

$$\frac{dx}{dt} = k\frac{a - x}{x}$$

[1] *J. Chem. Soc.*, 99, 95 (1911); Senter and Porter, *ibid.*, 99, 1049 (1911).

[2] Allgemeine Chem., 2, 11, 270.

[3] See Senter, *loc. cit.*; Müller, *Z. physik. Chem.*, 41, 483 (1902).

is ordinarily used. On Titoff's view, the rate of reaction is proportional to the concentration of positive catalyst; the negative catalyst can affect the reaction only by combining with the positive catalyst. We can represent this as follows:

$$C + N \rightleftharpoons NC,$$

where C is the positive catalyst, N is the negative catalyst and NC is an inert compound. The mass action law states that

$$[C] = K\frac{[NC]}{[N]}.$$

Now, if the concentration of NC is high compared to C or N, then the rate of the reaction will be inversely proportional to the concentration of the negative catalyst.

There are undoubtedly many examples in which the negative catalyst acts by suppressing the activity of a positive catalyst; it is readily conceivable that 10^{-7} M brucine hydrochloride could appreciably reduce the rate of oxidation of sodium sulfite since the rate is appreciably accelerated by 10^{-13} N copper sulfate. Similarly, the reduction in the catalytic activity of a weak acid by one of its salts, and the inhibitory power of water on acid-catalyzed reactions in alcohol can be explained as a reduction in the concentration of catalyst brought about by the weak acid salt or the water.

In a recent memoir on the subject of negative catalysis,[1] Taylor points out that a negative catalyst may also react with one of the constituents of the reaction under investigation; on such a basis a satisfactory explanation may be found for a number of reactions for which, hitherto, no adequate explanation has been forthcoming. The following list consists of such reactions: the inhibitory powers of a wide variety of substances, organic and inorganic, in the autoxidation of various organic compounds such as benzaldehyde, styrolene, oils, fats, rubber, resins and animal tissues; the inhibitory power of ether on the slow oxidation of various magnesium alkyl halides of the Grignard type; the inhibitory power of water on the decomposition of oxalic acid in sulfuric acid solutions,[2] on the velocity of conversion of acetophenoxime to acetanilide in concentrated sulfuric acid solutions, and on the decomposition of tri-ethyl sulphine bromide in acetone. These examples of inhibition may all belong to a type of negative catalysis in which the inhibitor combines with one of the reactants to form a molecular compound which subsequently decomposes, regenerating inhibitor and reactant unchanged. For marked inhibition to occur, the rate of reaction between inhibitor and reactant must be rapid as compared with the rate of the inhibited reaction; the rôle of the inhibitor in all these reactions would therefore be that of a competitor for one of the molecular species undergoing change.

[1] *J. Phys. Chem.*, **27**, 322 (1923).

[2] Bredig and Lichty, *J. Phys. Chem.*, **11**, 255 (1907).

Perhaps the most striking aspect of these reactions is the profound modification of the velocity by minute traces of inhibitor; Taylor cites an example in which under a given set of conditions a sample of redistilled benzaldehyde absorbed 2 cc. of oxygen per minute; the same amount of benzaldehyde containing 0.001 M hydroquinone absorbed less than 0.005 cc. per minute under the same conditions. The 2 cc. represents approximately 5×10^{19} molecules of oxygen or the equivalent number of benzaldehyde molecules reacting per minute. The total amount of hydroquinone present was about 0.005 g. which represents 3×10^{19} molecules approximately; therefore, sufficient hydroquinone molecules are present to form an equimolecular compound with all of the benzaldehyde molecules normally proceeding to reaction in one half minute. This is regarded as providing an explanation of the negative catalysis, for the rate of molecular compound formation is known to be so rapid as to be beyond our present methods of measurement, and therefore, even with such low concentrations of inhibitor as above indicated, there is an adequate number of molecules of inhibitor present to interact in stoichiometrically simple ratios with the molecules which would have reacted normally in the same time interval.

The hypothesis of molecular compound formation between inhibitor and one of the reactants as an explanation of the inhibitory power receives considerable support from the fact that in many cases such compounds have been isolated; phenolic substances, trichloracetic acid and stannic chloride which are all inhibitors of the autoxidation of benzaldehyde also form isolable double compounds with it; furthermore, inhibitory power often parallels capacity to form a double compound with a reactant. However, extent of compound formation alone is no criterion of inhibitory power because many examples are known in which a powerful inhibitor shows a less degree of compound formation than a weak inhibitor. This is explained in the following manner: suppose that the inhibitor B combines with one of the reactants A, giving the compound AB; we have then

$$A + B \rightleftarrows AB$$

and the equilibrium constant is

$$K = \frac{[AB]}{[A] \times [B]}.$$

For successful inhibitory power, it is postulated, firstly that the value of K be fairly small so that the equilibrium concentration of A is large and secondly that the rate of the reaction $A + B$ shall be very rapid; these two factors determine the inhibitory power. On the basis of these views Taylor has explained the negative catalytic effect of water on reactions occurring in strong sulfuric acid.

More recently another explanation [1] for negative catalysis has been given, based on the postulate that the examples discussed are really chain reactions,

[1] Christiansen, *J. Phys. Chem.*, **28**, 145 (1924).

that is, that the heat of the reaction between two reacting molecules is possessed by the resultant molecules and these very "hot" molecules can activate molecules of the reactants at the first encounter. When these react, the resultants in their turn can activate, and so on; the inhibitor is supposed to act by breaking these chains.[1]

Christiansen gives a preliminary discussion of the mechanism of bimolecular reactions based on the radiation hypothesis; the first condition for a reaction to occur is a collision between two molecules; for reactions which proceed with measurable speed only a minute fraction of the colliding pairs of molecules react, so that the number of effective collisions is equal to the product of the total number of collisions multiplied by the probability for a pair of molecules to have the required energy. This is expressed by the equation

$$v = se^{-E/RT},$$

where E is the critical increment. On this basis the explanation given by Taylor is denied, for it is assumed that a small quantity of a foreign gas cannot alter appreciably either the total number of collisions or the energy distribution of the colliding molecules. According to Christiansen the reactions in question are really chain-reactions in which the occurrence of one elementary reaction gives rise to a whole series of such reactions; evidently the velocity of a chain-reaction is equal to the number of chains starting per second multiplied by the number of links in each chain; the number of chains starting per second is of course the number of effective colisions per second and is not influenced appreciably by the presence of foreign molecules, but the number of links in a chain depends on the probability of breaking a chain, and this probability can be altered considerably by the presence of minute quantities of foreign molecules which can take up the energy from the "hot" molecules or react with them in some way. This is a plausible explanation of negative catalysis from which it is possible to conclude that when homogeneous reactions are inhibited by minute quantities of a foreign substance they are probably chain reactions.

We have therefore three possible explanations for the mechanism of negative catalysis, first, that the inhibitor combines with a positive catalyst; second, that the inhibitor combines with one of the reactants, and third, that inhibited reactions are really chain reactions in which the inhibitor acts by breaking the chains; it is not possible at present to decide between the views.

Hydrolysis and Esterification: In spite of the large number of studies made, the mechanism of these reactions is not yet known with any degree of certainty. In this section, the following mechanism will be used although other suggested mechanisms will be discussed. It is assumed that these reactions are really examples of successive reactions and that the active catalyst is the unhydrated hydrogen ion; therefore, on this basis the following equations represent the hydrolysis of ethyl acetate in aqueous solution:

$$CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOC_2H_5.H_2O, \qquad (1)$$

$$CH_3COOC_2H_5.H_2O + H^+ = CH_3COOH + C_2H_5OH + H^+. \qquad (2)$$

[1] See Bodenstein, *Z. physik. Chem.*, **85**, 346 (1913); *idem*, *Z. Elektrochem.*, **22**, 63 (1916); Weigert and Kellermann, *ibid.*, **28**, 456 (1922); Gohring, *ibid.*, **27**, 511 (1921).

Reaction (1) is supposed to be extremely rapid and (2) is supposed to be a slow reaction proceeding at a measurable rate; the equilibrium concentration of the ethyl acetate hydrate is assumed to be very small. If we consider the reaction catalyzed by hydrochloric acid, we must consider also the following equilibria:

$$HCl + nH_2O \rightleftarrows (H.aH_2O)^+ + (Cl.bH_2O)^-, \quad (3)$$

$$(H.aH_2O)^+ \rightleftarrows H^+ + aH_2O. \quad (4)$$

It is evident that the observed kinetics of the hydrolysis may be explained on the basis of these equations: in dilute aqueous solution the equilibrium concentration of the ethyl acetate hydrate will be proportional to the total concentration of ethyl acetate at any moment and similarly the concentration of the unhydrated hydrogen ion is proportional to the total acid concentration; consequently, in dilute aqueous solution the velocity of the slow reaction (2) will be proportional to the concentrations of total ethyl acetate and total acid. In more concentrated solutions these simple proportionality factors will evidently no longer hold and new velocity constants will be obtained for concentrated solutions; it will not be possible to predict the amount of this change without some independent method of measuring the concentrations of ethyl acetate hydrate and dry hydrogen ion. Ostwald [1] found that, using 1.6 *N* hydrochloric acid as catalyst, the velocity constant for methyl acetate increased from 19.9 in dilute solution to 24.2 when the concentration of methyl acetate was about 1.5 *M*. The mechanism suggested in the foregoing discussion may be applied to hydrolytic reactions generally such as the hydrolysis of sugars, esters or amides. Stieglitz [2] suggests the following mechanism for hydrolytic reactions: he postulates that the ester, which is regarded as a weak base, first forms an oxonium salt with the catalyzing acid before undergoing hydrolysis; this salt ionizes, and the positive ion is the reacting substance; the catalytic action of the acid is due to the formation of larger amounts of the ion, since the salt would ionize more extensively than the weak base. Stieglitz studied the hydrolysis of imido-esters, in which the imido group (: NH) replaces the oxygen atom of the ordinary esters. The following equations represent the action for methyl imido-benzoate:

$$C_6H_5C(:NH)OCH_3 + HCl \rightleftarrows [C_6H_5C(:NH)OCH_3.HCl],$$

$$[C_6H_5C(:NH)OCH_3.HCl] \rightleftarrows [C_6H_5C(:NH)OCH_3.H]^+ + Cl^-,$$

$$[C_6H_5C(:NH)OCH_3.H]^+ + H_2O \rightleftarrows C_6H_5COOCH_3 + NH_4^+.$$

Recently attempts have been made to replace volume concentrations of the reactants by their activities or thermodynamic concentrations [3] (Chap. XII).

[1] *J. prakt. Chem.*, **28**, 449 (1883).

[2] *Am. Chem. J.*, **39**, 29, 402 (1908); *J. Am. Chem. Soc.*, **35**, 1774 (1913).

[3] Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920); Clarke, *J. Am. Chem. Soc.*, **43**, 1759 (1921); Scatchard, *ibid.*, **43**, 2387, 2406 (1921); **45**, 1580, 1716 (1923); Fales and Morrell, *ibid.*, **44**, 2071 (1922); Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922); Åkerlof, *Z. physik. Chem.*, **98**, 260 (1921).

These calculations, however, depend on the particular mechanism selected and we are by no means certain of these, as is shown by the great variety of mechanisms selected by different workers. Fales and Morrell studied the hydrolysis of cane sugar and showed that the velocity of inversion by hydrochloric acid is proportional to the thermodynamic concentration of hydrogen ion only between 0.01–.001 *M* HCl. Moran and Lewis in a similar study obtained constant velocity coefficients for the hydrolysis of sucrose over the range 0.3–2.0 *M* by assuming that the velocity is proportional to the activities of the sucrose, water and hydrogen ion participating. It was necessary, however, to assume that the sucrose is present in the solution mainly as a tetrahydrate and that the reactants are a sucrose dihydrate and the hydrogen ion; the activity of the hydrogen ion is assumed to be largely influenced by the viscosity of the medium. Scatchard concludes that the inversion of sucrose is of the sixth order with respect to water and that the speed of the reaction is independent of the viscosity of the solution.

The fact that the hydrolysis of esters of strong acids is not catalyzed by hydrogen ions is discussed in a recent paper [1]; esters of inorganic acids such as phosphoric acid, sulphonic acid, sulfuric acid, hydrochloric and nitric acid are not hydrolyzed by hydrogen ions. Experiments on the rate of hydrolysis of benzyl chloride, monochorhydrin, butyl chloride and ethyl nitrate showed that hydrogen ions have no effect on the rate and this behavior is common to all esters derived from strong mineral acids. Additional experiments showed that this was true for esters of strong organic acids because hydrochloric acid only feebly accelerated the rate of hydrolysis of methyl trichloracetate. Senter [2] has shown that the hydrolysis of chloracetic acid is not catalyzed by a strong acid; Sudborough [3] has shown that esters of strong acids are fairly easily hydrolyzed by water. Olivier and Berger conclude that the stability of strong acid esters is due to their inability to form the oxonium salts postulated by Stieglitz.

The esterification of strong acids shows similar abnormalities, since Sirks has found [4] that weak organic acids esterify more quickly than stronger acids in presence of hydrochloric acid, but the opposite occurs when there is no added catalyst.

A large number of studies have been made on the acid hydrolysis of fatty acid esters and it is noteworthy that they [5] have approximately all the same temperature coefficients, $k_{35}/k_{25} = 2.4$.

The hydrolysis of substituted fatty esters has been very completely studied; the acid hydrolysis of the halogen substituted esters may be represented by

[1] Olivier and Berger, *Rec. trav. chim.*, **41**, 637 (1922).

[2] *J. Chem. Soc.*, **91**, 460 (1907).

[3] *J. Chem. Soc.*, **101**, 1236 (1912).

[4] *Rec. trav. chim.*, **27**, 248 (1908).

[5] Ostwald, *J. prakt. Chem.*, **28**, 449 (1883); de Hemptinne, *Z. physik. Chem.*, **13**, 561 (1894); Lowenherz, *ibid.*, **15**, 397 (1894); Kastle and Keiser, *Am. Chem. J.*, **15**, 471 (1893); Lamble and Lewis, *J. Chem. Soc.*, **105**, 2330 (1914); Griffith, Lamble and Lewis, *ibid.*, **111**, 389 (1917); Taylor, *J. Am. Chem. Soc.*, **37**, 551 (1915); Harned and Pfanstiel, *ibid.*, **44**, 2193 (1922).

the following equation in the case of ethyl chloracetate:

$$CH_2ClCOOC_2H_5 + H_2O \rightleftarrows CH_2ClCOOH + C_2H_5OH.$$

Preliminary experiments showed that there was no appreciable splitting of halogen either from the ester or the acid during the course of the experiment.[1] The introduction of a halogen in the α position lowers the rate of hydrolysis: taking the rate of hydrolysis of ethyl acetate at 25° C. as 100, chloracetic ester is 64 and bromacetic ester is 76; the introduction of the halogen in all cases diminished the velocity, the diminution being greater in the β substituted compounds; the temperature coefficient of the α substituted esters is 2.0 and of the β substituted esters is 2.4, the same as the unsubstituted esters. The hydrolysis of ethyl cyanacetate and its homologues in acid solution gave results similar to the halogens but [2] the reduction in velocity was greater; unlike the halogens, the α cyanogen group retards the velocity more than the β cyanogen group; the temperature coefficients are all about 2.4. The action in acid solution is represented by the following equation:

$$CH_2CNCOOC_2H_5 + H_2O \rightleftarrows CH_2CNCOOH + C_2H_5OH.$$

The acid hydrolysis of hydroxy-acid esters and alkyloxy acetic acid esters showed that, in practically all cases,[3] the effect of substitution was to diminish the velocity; substitution in the β position produces greater retardation than in the α position; the temperature coefficients were about 2.4 in all cases.

The alkaline saponification of ethyl acetate seems to have been measured first by Warder [4]; this study was followed by a series of very accurate and comprehensive measurements by Reicher.[5] He determined the relative effects of various bases and also showed that the effect of the alcohol radical in the ester is practically constant. Methyl esters decompose most rapidly and the velocity decreases as the ester becomes more complex. The differences, however, are exceedingly slight beyond about the first three members. Reicher's experiments with the esters of different acids pointed toward a decrease in velocity with increasing molecular weight. The temperature coefficient for the alkaline hydrolysis of esters is $k_{35}/k_{25} = 1.82$ as compared with 2.4 for the acid hydrolysis. The effect of substitution of hydroxy and alkyloxy groups is to increase greatly the rate of saponification by alkali [6]; taking ethyl acetate to be 100, the following results were obtained at 25° C.: ethyl glycollate 1000, ethyl methyloxy acetate 1950, ethyl ethyloxy acetate 990, ethyl propionate 90,

[1] Drushel and Hill, *Am. J. Sci.*, **30**, 72 (1910); Drushel, *Am. J. Sci.*, **34**, 69 (1912); Bevan, *Proc. Camb. Phil. Soc.*, **13**, 269 (1906).

[2] Drushel, *Am. J. Sci.*, **33**, 27 (1912); **37**, 514 (1914).

[3] Drushel and Dean, *Am. J. Sci.*, **34**, 293 (1912); **35**, 486 (1913); Drushel, *ibid.*, **39**, 113 (1915).

[4] *Ber.*, **14**, 1361 (1881).

[5] *Ann.*, **228**, 257 (1885); **232**, 103 (1886).

[6] Dean, *Am. J. Sci.*, **35**, 605 (1913); **37**, 331 (1914); Findlay and Turner, *J. Chem. Soc.*, **87**, 747 (1905); Findlay and Hickmans, *ibid.*, **95**, 1004 (1909).

ethyl lactate 997 and ethyl glycerate 870. The temperature coefficients were all about 5.3 for k_{25}/k_0 which gives Q = 10,800 as compared with 10,950 for the alkaline hydrolysis of ethyl acetate.

A number of investigations on the hydrolysis of amides have been made [1] but the results are not in good agreement; from Crocker's results we obtain k_{35}/k_{25} = 3.14 for the acid hydrolysis of acetamide; Salo Kilpi confirmed this, but Euler and Rudberg obtained the value 2.4; Peskoff and Meyer obtained erratic values for different amides, the mean being 2.86. For the alkaline hydrolysis of amides Crocker obtained k_{35}/k_{25} = 1.5 (calculated) whereas Peskoff and Meyer obtain a mean value of 2.65. Reid [2] measured the rate of hydrolysis of benzamide by alkali at 100° and 25° C.; from his results the value of Q is 14,800 whence k_{35}/k_{25} = 2.25; he also found that with the homologues of benzamide, substitution diminishes the rate of hydrolysis in acid solution, ortho substitution having the greatest effect; in alkaline solution, substitution produced a much wider range of velocities, ortho substitution usually diminishing the velocity. The esterification of amides in absolute alcohol is interesting because, when an acid catalyst is present, the reaction rate is greatly diminished by small amounts of water. The matter is not complicated by the formation of water during the reaction since the following equation represents the reaction in the case of benzamide:

$$C_6H_5CONH_2 + C_2H_5OH \rightleftarrows C_6H_5COOC_2H_5 + NH_3.$$

Reactions of Halogen Substituted Organic Compounds: The alkyl halides react in a number of ways at a measurable rate and several of these reactions have been studied carefully; however, in spite of their importance in organic chemistry, the literature is not very extensive, especially when compared with that on ester hydrolysis or sugar inversion. Alkyl halides and sodium thiosulfate react in dilute aqueous solution [3] and the action using ethyl iodide may be represented as follows:

$$C_2H_5I + S_2O_3^{--} = C_2H_5.S_2O_3^- + I^-.$$

Slater showed that the reaction is practically complete in the direction indicated and is substantially free from secondary reactions; it is bimolecular, the velocity being proportional to the concentration of the halide and to the concentration of the thiosulfate ion. A puzzling exception to this is shown by certain ethylene derivatives, with some of which ($C_2H_4I_2$, C_2H_4IBr, $C_2H_4Br_2$) the change proceeds as a bimolecular reaction, whilst with others (C_2H_4BrCl, C_2H_4ICl) the reaction appears to be unimolecular, the velocity in this case being independent of the thiosulfate concentration. He also showed that neutral salts containing a common ion diminish the velocity, the opposite effect to that obtained in

[1] Crocker, *J. Chem. Soc.*, **91**, 593, 955 (1907), Salo Kilpi, *Z. physik. Chem.*, **80**, 165 (1912); Peskoff and Meyer, *ibid.*, **82**, 129 (1913); Euler and Rudberg, *Z. anorg. Chem.*, **127**, 244 (1923).

[2] *Am. Chem. J.*, **21**, 284 (1899); **24**, 397 (1900).

[3] Slater, *J. Chem. Soc.*, **85**, 1286 (1904); **87**, 481 (1905); Slater and Twiss, *ibid.*, **95**, 93 (1909)

acid catalysis; it is significant that in all the cases investigated the temperature coefficient of the reaction between alkyl halides and sodium thiosulfate is 3 within experimental error. The iodide ion catalyzes the decomposition of alkyl halides [1] according to the following equation:

$$C_2H_4I_2 + I^- = C_2H_4 + I_2 + I^-.$$

The velocity is proportional to the concentration of the halide and to that of the iodide ion and the temperature coefficient $k_{35}/k_{25} = 2.5$.

Alkyl iodides also react with organic bases as represented by the following equation:

$$C_2H_5I + (C_2H_5)_3N = (C_2H_5)_4NI.$$ [1]

The temperature coefficient has been measured in very few of the studies, but appears to have approximately the same value in all cases, namely, $k_{35}/k_{25} = 2.2$; the average deviation from this value is usually 4–5 per cent and the maximum deviation is very rarely 10 per cent; since the analytical difficulties in this work are great, the variations observed are probably within experimental error. Hawkins measured the velocity and temperature coefficients of the reaction between allyl bromide and pyridine in seven solvents; from his results we obtain a mean value for $k_{35}/k_{25} = 2.10$. Preston and Jones who studied the reaction of allyl bromide with dimethyl aniline and tri-isoamylamine obtained a mean value for $k_{35}/k_{25} = 2.28$.

The reaction between silver nitrate and alkyl iodides is still very puzzling in spite of several comprehensive investigations [2]; this is partly because the reaction is not the simple one represented by the following equation:

$$C_2H_5I + AgNO_3 = AgI + C_2H_5NO_3$$

but is complicated by at least two other reactions:

$$AgNO_3 + C_2H_5I + C_2H_5OH = AgI + (C_2H_5)_2O + HNO_3,$$
$$AgNO_3 + C_2H_5I + H_2O = AgI + C_2H_5OH + HNO_3.$$

The reaction is bimolecular and since the velocity constant is increased either by increasing the concentration of silver nitrate or by the presence of alkali nitrates, it is probable that the non-ionized silver nitrate is the reactant; the products of the reaction, nitric acid, ethyl nitrate and ether have no effect on the velocity.

The reaction between α-bromo fatty acids and silver nitrate has been studied by Senter; [3] the equation representing the change is:

$$CH_3CHBrCOOH + AgNO_3 + H_2O = CH_3CHOHCOOH + AgBr + HNO_3.$$

[1] Menschutkin, *Z. physik. Chem.*, **5**, 589 (1890); Menschutkin and Vasileff, *J. Russ. phys. Chem. Soc.*, **22**, 346 (1892); Clarke, *J. Chem. Soc.*, **97**, 416 (1910); Long, *ibid.*, **99**, 2164 (1911); Preston and Jones, *ibid.*, **101**, 1930 (1912); Hawkins, *ibid.*, **121**, 1170 (1922).

[2] Lengfeld, *Am. J. Sci.*, **11**, 40 (1889); Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1900); *ibid.*, *Z. physik. Chem.*, **69**, 148 (1909); Donnan and Potts, *J. Chem. Soc.*, **97**, 1882 (1910).

[3] *J. Chem. Soc.*, **97**, 346 (1910).

He made the remarkable observation that reactions of this type are markedly accelerated by the silver halide. He appears to assume that the whole of the precipitated silver halide is active catalytically: "Unfortunately an accurate investigation of the effect is rendered very difficult by the fact already mentioned, that the precipitate soon coagulates and is withdrawn from the sphere of action by rising to the top or sinking to the bottom of the solution." It is possible, however, that the minute quantity of dissolved iodide ion catalyzes the reaction between ethyl iodide and silver nitrate and it would be desirable to know whether those influences which affect the velocity, affect also the solubility of the silver halide.

CHAPTER XV

REACTION VELOCITY IN HETEROGENEOUS SYSTEMS

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The study of reaction kinetics in heterogeneous systems is concerned with the rate of processes occurring at the interface between two phases. All types of such study are known at solid-solid, solid-liquid, liquid-liquid, liquid-gas and solid-gas interfaces. The rate of solution of a solid in a liquid, with or without chemical reaction, is an example of the solid-liquid type. Pronounced differences in reaction rate have been observed. Cadmium sulphate crystals dissolve very much more slowly in water than do zinc sulphate crystals under like experimental conditions.[1] Zinc dissolves much less rapidly in hydrochloric acid solution than it does in the same solution containing dissolved nitrobenzene or benzaldehyde.[2] Measurement of the rate of hydrolysis of insoluble esters in either acid or alkaline aqueous media is an example of liquid-liquid interface phenomena studied by Lowenherz, Goldschmidt and others.[3] The rate of evaporation of a liquid is perhaps the simplest example that could be studied of a liquid-gas interface phenomenon. The rate will be dependent on the nature of the liquid surface and on the gas pressure in the gas space if not on other variables. Similarly, evaporation from a solid surface is a simple example of a process occurring at a solid-gas interface. To this latter class, however, belong many of the very important reactions obtaining in the subject of contact catalysis. The dissociation of a solid to yield a gas and a solid dissociation product can be shown to be a phenomenon occurring at a solid-solid interface. Many reactions between gases and solids similarly occur at solid-solid interfaces. The study of the kinetics of such varied processes is, therefore, of the utmost importance in the determination of mechanism in a large number of familiar phenomena of theoretical and practical interest.

It will be evident as the result of a little consideration that two factors are always involved in the velocity of such heterogeneous reactions. The net velocity of reaction will be dependent on the rate at which the chemical or physical change itself occurs in the interface region and also on the rate at which the products of the process are removed from the interface region into the surrounding medium. This latter is determined by the rate of diffusion of the reaction products from the interface region into the surroundings. Now,

[1] Observation of Professor G. A. Hulett, Princeton University.

[2] *Proc. K. Akad. Weten. Amsterdam*, **23**, 1449 (1921).

[3] Lowenherz, *Z. physik. Chem.*, **15**, 389 (1894).
Goldschmidt, *Z. physik. Chem.*, **31**, 235 (1899).

since the net tempo of a whole process consisting of successive stages is determined at the steady state by the tempo of the slowest stage, it follows that, in the kinetics of heterogeneous reactions, different features will be met according as the actual chemical or physical process is faster or slower than the diffusion of the reaction products away from the interface. If the chemical process be faster, the diffusion process will set the reaction speed. If the chemical process be slower, the chemical reaction will be the determining factor. It is necessary therefore in analyzing the kinetics of reaction in heterogeneous systems to consider in some detail the laws governing diffusion and those obtaining for chemical reaction at an interface.

The Laws of Diffusion: Graham enunciated the law of diffusion for gases. Gases diffuse at rates which are inversely proportional to the square roots of their densities, a conclusion which has already been shown to be in harmony with the kinetic theory of gases. Hydrogen therefore will diffuse away from an interface four times more rapidly than oxygen, provided the concentration gradient in the two cases is the same. This law holds true irrespective of the fluid medium through which the gases diffuse. Thus, Carlson [1] determined the ratio of the diffusion velocities of carbon dioxide and oxygen in water by measuring the velocity of solution of these gases in water under comparable conditions. He obtained a value of 1.158 in good agreement with the theoretical value

$$\frac{D_{O_2}}{D_{CO_2}} = \sqrt{\frac{44}{32}} = 1.173$$

and with a direct measurement of the rate of diffusion of the two gases in water [2] which gave the quotient 1.166.

The diffusion coefficient of one gas in another gas is calculable according to the kinetic theory of gases. Into the details of this calculation we have not here space to proceed. Reference must be made to the larger texts on the subject.[3] Meyer's formula for the diffusion coefficient is

$$D = \frac{1}{3n}(\bar{u}_1 l_1 n_2 + \bar{u}_2 l_2 n_1),$$

where D is the diffusion coefficient, n the number of molecules per cc., n_1 and n_2 the numbers of each species, $\bar{u}_1^2$ and $\bar{u}^2$ the mean square velocity, l_1 and l_2 the mean free path of the respective molecules.

From this formula it may be deduced that the coefficient is inversely proportional to the pressure since $D \propto \frac{1}{n}$. Further, since $\bar{u}_1$ and $\bar{u}_2$ are propor-

[1] *Medd. Vet-Akad. Nobel Inst.*, 2, No. 5 (1911).

[2] *Medd. Vet-Akad. Nobel Inst.*, 2, No. 6 (1911). See also: Stefan, *Sitzber. Wien. Akad.*, 77, 37 (1878); Hufner, *Wied. Ann.*, 60, 134 (1878).

[3] O. E. Meyer, *Kinetische Theorie der Gase* (1877), 1895, § 95.

Kuenen, Ostwald-Drucker, *Handbuch d. Allgemein Chem.*, III, 1919, pp. 1–139. Leipsic. The following data are drawn from this source.

tional to $T^{1/2}$ and n is proportional to T^{-1}, D should therefore vary as $T^{3/2}$. The formula implies that D varies also as the composition of the mixture, i.e., as n_1 and n_2 vary, which is not confirmed by experimental investigation. Kuenen [1] has suggested a modification of the Meyer formula which decreases the variability of D due to variation in composition.

From another standpoint entirely Stefan [2] has formulated the dependence of D on the kinetic magnitudes by means of an equation

$$D = \frac{3}{16}\frac{1}{n\sigma^2} \cdot \frac{1}{\sqrt{\pi h}} \cdot \frac{m_1 + m_2}{m_1 m_2},$$

where σ is the distance of the centers of the two molecules at collision and is therefore equal to $\frac{1}{2}(S_1 + S_2)$, where S is the molecular radius,

$$m_1 \bar{u}_1^2 = m_2 \bar{u}_2^2 = \frac{4}{\pi h}$$

and m_1 and m_2 are the respective masses of the molecules. In this formula D is independent of n_1 and n_2 in agreement with experimental results.

Experiment in general [3] has shown that D is inversely proportional to the pressure. Loschmidt [4] found the following values for D at atmospheric pressure by means of the formula

$$D_{760} = \frac{D_{\text{obs.}} \times p_{\text{obs.}}}{p_{760}},$$

where the observations were made on several gases at varying pressures. The data will also serve to give an orientation into the magnitude of the diffusion velocity.

TABLE I

DIFFUSION COEFFICIENTS OF GASES IN MIXTURES

Gas Mixture	D_{760} from $D_{\text{obs.}}$ at Operating Pressures of			
	760	510	360	310 mm.
CO_2–Air	0.142	—	0.144–0.146	0.142–0.143 cm./sec.
CO_2–H_2	0.556	0.551	—	
H_2–O_2	0.715	0.715	—	

The most accurate experiments show a small variation of D with gas composition, n_1/n_2. The influence of temperature is generally expressed by means of an equation

$$D \propto T^x.$$

[1] *Loc. cit.*, pp. 41, 42.

[2] *Wien. Sitz. ber.*, **65**, 323 (1872): Kuenen, *loc. cit.*, p. 43.

[3] For literature see Kuenen, *loc. cit.*, pp. 121–129.

[4] *Wien. Sitz. ber.*, **61**, 367; **62**, 468 (1870).

The exponent x varies considerably. It is approximately 1.7 for gases (Theory requires $T^{3/2}$). For vapors it approaches 2.[1]

Graham's studies of diffusion in aqueous solutions established the dependence of the rate of diffusion on the substance diffusing. He furthermore showed that diffusion increased strongly with increase of temperature. In dealing with the physical factors controlling the reversibility of chemical reactions, Berthollet had expressed his belief [2] that the rate of diffusion was determined in part by the concentration gradient of the substance diffusing in the solution. The exact mathematical relationship involved in this process was formulated by Fick [3] and tested experimentally. According to Fick's Law, the quantity of substance dS which passes in time dt through a diffusion cylinder of cross section q under a concentration gradient $\frac{dc}{dx}$ (i.e., a concentration c of the cross section at a point x and one of $c + dc$ at $x + dx$) is given by the equation

$$dS = - Dq \frac{dc}{dx} dt.$$

D is a constant for a given substance and may be termed the diffusion coefficient. As to the nature of the force determining diffusion in solution, Nernst [4] pointed out that it was essentially the same force which, in the theory of solutions, we term the osmotic pressure; that diffusion in solutions was comparable with gaseous diffusion, but enormously slower, owing to the enormous resistance friction. From the value of the mechanical force obtainable by osmotic pressure measurements in the case of cane sugar and from the measured rate of diffusion of cane sugar through water, Nernst was able to show that the resistance friction was so great that it requires a force equal to 4.7×10^9 kg. weight to drive one gram molecule of cane sugar through water with a velocity of 1 cm. per second.

With salts dissociated in solution into ions the problem is somewhat more complex. At first, it might be thought that independent diffusion of the ions might occur. If this were possible, fast-moving ions such as hydrogen ions would diffuse more rapidly than slower ions such as chloride ions, since, as conductivity measurements reveal, these ions have different mobilities. The separation of ions set up as a result of such differing rates of diffusion would, however, bring about the production of electrostatic forces which would tend to retard the faster moving ions and speed up the slower ions. The opposing forces of diffusion and electrostatic attraction result in the ions diffusing through the solution at equal rates. With the aid of this concept, Nernst was able to show that the amount of salt diffusing in a given time could be expressed

[1] For tables of diffusion coefficients at various temperatures see Landolt-Bornstein Tabellen, 1912, pp. 136-138.

[2] Chemical Affinity, 1805.

[3] *Pogg. Ann.*, **94**, 59 (1855).

[4] *Z. physik. Chem.*, **2**, 613 (1888).

in terms of the mobilities of the ions, the cross-sectional area of the diffusing medium and the concentration gradient. In a diffusion cylinder of cross section q containing a dissociated electrolyte of concentration c, let the osmotic pressure be p; in the diffusion process let the concentration be $c - dc$ and the osmotic pressure $p - dp$ at a distance dx from the solution of concentration c. The volume $q \cdot dx$ then contains $cq \cdot dx$ gram mols. The force acting upon this salt is $q \cdot dp$. Hence the force per gram mol. is $\frac{1}{c} \cdot \frac{dp}{dx}$. Let us assume the ions to migrate first under the influence of osmotic pressure alone. The quantities of the two ions migrating in time dt through a cross section of the diffusion cylinder, for two ions of mobilities U and V, are respectively

$$-Uqc\left(\frac{1}{c}\frac{dp}{dx}\right)dt \qquad \text{and} \qquad -Vqc\left(\frac{1}{c}\frac{dp}{dx}\right)dt.$$

The electrostatic forces which come into play as a result of such osmotic diffusion will be respectively per gram ion

$$-\frac{dE}{dx} \qquad \text{and} \qquad +\frac{dE}{dx},$$

where E is the electrostatic potential. The migration through the cross section as a result of these forces of attraction and repulsion will be respectively

$$-Uqc\frac{dE}{dx}dt \qquad \text{and} \qquad +Vqc\frac{dE}{dx}dt.$$

Now, with equal rates of diffusion for the two ions under the combined influence of osmosis and electrostatic attraction, it follows that

$$-Uqdt\left(\frac{dp}{dx} + c\frac{dE}{dx}\right) = -Vqdt\left(\frac{dp}{dx} - c\frac{dE}{dx}\right) = dS.$$

whence, by elimination of $\frac{dE}{dx}$,

$$dS = -\frac{2UV}{U+V}q\frac{dp}{dx} \cdot dt.$$

and, since $p = cRT$,

$$dS = -\frac{2UV}{U+V}RTq\frac{dc}{dx}dt.$$

Comparing this equation with that expressing Fick's Law for non-electrolytes, it follows that the diffusion coefficient, D, for an electrolyte is given by the equation

$$D = \frac{2UV}{U+V}RT.$$

A similar equation has been developed by Noyes and published by Haskell [1] for the general case of a salt dissociating into $n_c + n_a$ cations and anions.

The most comprehensive study of diffusion coefficients of salt solutions has been carried out by W. Öholm [2] in a wide concentration range and for a variety of salts. The appended table illustrates the agreement of the experimental values for D and those calculated on the basis of the Nernst theory. The data apply to solutions at a concentration of 0.01-normal, at which concentration, in the case of all the substances quoted, with the exception of acetic acid, dissociation is approximately complete.

TABLE II

DIFFUSION OF ELECTROLYTES

Substance	D 18° obs.	D 18° calc.	Substance	D 18° obs.	D 18° calc.
KCl	1.460	1.460	KOH.....	1.903	2.109
NaCl..... .	1.170	1.173	NaOH.....	1.432	1.558
LiCl..... .	1.000	0.994	KI.....	1.460	1.467
HCl...	2.324	2.431	CH_3COOH ...	0.93	1.37

Öholm's results show that the rate of diffusion increases with increasing dilution. Thus, for a 1-normal KCl solution, D (18°) = 1.330; for a 0.01-normal solution, the value has increased to 1.460. In the later work, the substitution of a brass diffusion apparatus for the glass vessels hitherto used permitted the examination of diffusion in solutions of great viscosity differences. Thus, for 1-normal KCl in 1.5-normal sugar solution, the value for D decreases to 0.42 while in a 2-normal sugar solution, the diffusion coefficient sinks to 0.22. Similar reductions in the rate of diffusion are obtained with glycerine as the viscous medium.

A recent publication by Cohen and Bruins [3] records a refinement of experimental procedure in the investigation of the velocity of diffusion in solutions, applicable alike to aqueous and non-aqueous solutions. The process is suited to experiments in a wide temperature interval. It yields "true" diffusion coefficients because, during an experiment, the change in concentration is small. The reproducibility of the results attained has been improved so that differences of a few tenths of one per cent in aqueous solutions are usual as contrasted with the 2 per cent variations more usual hitherto. An absolute accuracy of 0.3 per cent is claimed for the results. The analysis of the diffusion layers is effected by means of a Zeiss-Rayleigh-Löwe water-interferometer adapted when necessary to solutions in organic solvents. The paper contains a critical survey of the general literature of the subject of diffusion.

The Temperature Coefficient of Diffusion Processes: With lowering of working temperature the rate of diffusion falls. For strong electrolytes

[1] *Phys. Rev.*, **27**, 145 (1908).

[2] *Z. physik. Chem.*, **50**, 309 (1904); **70**, 378 (1910); *Medd. Vet-Akad. Nobel Inst.*, **2**, Nos. 23, 24, 26 (1912).

[3] *Z. physik. Chem.*, **103**, 349 (1922).

Öholm showed that the fall was approximately 2.5 per cent per degree lowering of temperature, a value in good agreement with that demanded by the Nernst theory. With substances having a higher resistance to diffusion, or, in other words, a lower rate of diffusion, which obtains with organic molecules of high molecular weight, the influence of temperature seems to increase and the temperature coefficient attains greater values. Thus, for sugar solutions, a temperature coefficient of 3.2 per cent per degree was obtained; for dextrin solutions the corresponding value attained 3.5 per cent.

Collecting a variety of experimental data on all types of aqueous solutions of electrolytes and non-electrolytes, Öholm compiled the following table for the approximate values of α, the temperature coefficient per degree, at various ranges of values of the diffusion coefficient D.

$D = 2.4$	2.0–1.8	1.6–1.4	1.2–1.1	0.8–0.7	0.4–0.3	0.2–0.1,
$\alpha = 0.0018$	0.020	0.022	0.025	0.029	0.035	0.040.

The temperature coefficient α was calculated from two measurements of the diffusion coefficient at two temperatures by means of the equation

$$\frac{D_2}{D_1} = 1 + \alpha(T_2 - T_1).$$

The temperature coefficient is apparently some function of the diffusion coefficient, a feature observed also by Kohlrausch [1] in the relationship of ionic mobility and its temperature coefficient. The greater the ionic mobility the less is the temperature coefficient. As far as solutions of electrolytes are concerned. the temperature coefficients of the two quantities are approximately the same. The magnitude of the temperature coefficient in both cases is apparently to be associated with the greater or less extent to which the motion of molecules or of ions is influenced by the concomitant motion of solvent molecules—for similar features occur in the investigation of non-aqueous solutions. In alcohol, for example, glycerine diffuses slowly and has a high temperature coefficient; chloroform and bromoform, much heavier molecules, diffuse much more rapidly and have low temperature coefficients. This points to extensive association of glycerine molecules with alcohol and relative freedom of the halogen compounds.

In the study of reaction kinetics it is more usual to express the temperature coefficient of reaction velocity as the fractional increase per 10° rise in temperature. Thus, in the preceding chapter, temperature coefficients of 2–4 per 10° rise have been frequently indicated for reactions in homogeneous systems. Now, since the criterion of temperature coefficient will be employed in the succeeding pages to test the nature of certain heterogeneous reaction velocity measurements with a view to determining the mechanism of the process, it will be useful to transpose Öholm's results to the 10° scale. Thus Öholm's α

[1] *Z. Elektrochem.*, **14**, 129 (1908).

= 0.025 per degree is transformed to a coefficient

$$\frac{D_{T+10}}{D_T} = 1.28.$$

This value is materially less than that characteristic of the temperature coefficients of the homogeneous reaction velocities previously discussed. The following data present the transposition of temperature coefficients of diffusion rates from the 1° to the 10° basis for the extremes and the mean temperature coefficients listed, according to Öholm, in the preceding table.

D =	2.4	1.2–1.1	0.2–0.1,
α =	0.018	0.025	0.040,
$\frac{D_{T+10}}{D_T}$	1.20	1.28	1.48.

For gaseous diffusion, the temperature coefficient per 10° rise will be even smaller than this, as a consideration of the equation developed for the mean velocity of a gas molecule (Chap. III, p. 75) will indicate. The following table gives values so calculated [1] for the mean velocities of a few gases at 0° and 20° C.

TABLE III

MEAN VELOCITY OF GAS MOLECULES

Gas	Mean Velocity × 10^{-5} cm. × $sec.^{-1}$	
	0°	20°
H_2	1.838	1.904
O_2	0.4613	0.4778
N_2	0.4928	0.5106
Air	0.4849	0.5023
Hg	0.1842	0.1908
CO_2	0.3933	0.4076
CO	0.4933	0.5109

Such low temperature coefficients are in agreement with Öholm's generalization in reference to the more viscous liquid media. High diffusion rate is accompanied by low temperature coefficient.

It is therefore evident that, in the examination of the temperature coefficient of reaction velocities in heterogeneous media, the occurrence of low values between 1 and 1.5 will tend to indicate that the predominant factor in determining reaction rate is the diffusion factor. On the other hand, high temperature coefficients will, in agreement with previous indications, point towards the chemical processes at work as the factor determining the rate of reaction. The implications of such a viewpoint will emerge in succeeding paragraphs.

Diffusion and Molecular Motion. The Stokes-Einstein Law Applied to Solutions: Assuming the independent motion of the several constituents of a

[1] Dushman, High Vacuum, p. 9. *Gen. Electric Rev.* (1922).

mixture, the relationship between molecular motion and diffusion is given by means of the equation

$$D = \frac{\overline{\Delta^2}}{2t}.$$

Here, D is the diffusion coefficient of the diffusing substance, $\overline{\Delta^2}$ is the mean square of the displacement which takes place in a given direction in time t. If one further assumes that the particles possess the same mean kinetic energy as a gas molecule at the same temperature, then the Einstein equation

$$\overline{\Delta^2} = \frac{2RT}{N} Bt$$

holds.[1] In this equation, R is the gas constant, T the absolute temperature, N the Avogadro number, B the mobility coefficient, that is, the velocity of motion of the given particle moving through the solution under the influence of unit force. By combining the above equations,

$$D = \frac{RT}{N} B.$$

Now, according to Stokes' Law, for spherical particles large compared with the molecules of solvent

$$= \frac{1}{6\pi\eta r},$$

where η is the viscosity of the solvent and r the radius of the solute molecule. Combining these equations we obtain

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r},$$

an equation the applicability of which to suspensions and emulsions is given in the chapter on colloids, the experimental results thereby obtained constituting strong evidence for molecular reality. Efforts have been made to apply this equation to diffusing molecules. Direct proof of the applicability of the equation in such cases is not possible. There are, however, several alternative methods of test: (*a*) In the same solvent, at the same temperature, with a variety of diffusing substances, the equation reduces to

$$D \cdot r = \text{constant},$$

whence, from the experimental measurements and values of r obtained in other ways, the equation may be tested. (*b*) At constant temperature a given substance diffusing in a variety of solvents gives a number of equations which all reduce to

$$D\eta = \text{constant}.$$

[1] *Ann. Physik*, (4) **17**, 549 (1905); **19**, 371 (1906); *Z. Elektrochem.*, **14**, 235 (1908).

Alternatively, one can use such determinations to ascertain whether the molecular radius remains constant. (*c*) Finally, by assuming r independent of temperature,

$$D\eta = KT,$$

whence, from measurements of diffusion and viscosity over a temperature range, the Stokes-Einstein equation may be tested. All these methods of test have been applied.[1]

The results of these investigations all point to the applicability of the Stokes-Einstein formula so far as the first approximation is concerned. In the latest research of Cohen and Bruins, the velocity of diffusion of tetrabromethane in tetrachlorethane as solvent was carefully studied in a temperature interval from 0 to 50° C., the viscosities being also obtained. A small deviation from the Stokes-Einstein law was observed which exceeds, however, the experimental error by at least three times. The deviation is such that the temperature coefficient is somewhat smaller than would be expected from the equation. The following table shows the results of such a test by Cohen and Bruins.

TABLE IV

DIFFUSION AND THE STOKES–EINSTEIN LAW

Temp.	D obs.	D calc. Stokes-Einstein	$r \times 10^8$ Stokes-Einstein
0° C.	0.300	(0.300)	2.15
10	0.385	0.385	2.15
15	0.429	0.431	2.16
25	0.527	0.531	2.17
35	0.633	0.643	2.18
50	0.811	0.833	2.21

REACTION VELOCITIES AT SOLID–LIQUID INTERFACES

Velocity of Solution: Guldberg and Waage in their classical studies on chemical affinity[2] investigated the rate of solution of metals in hydrochloric acid in an effort to associate mass action with reaction speed. They showed that increase of temperature brought about an increase in reaction velocity, the rate at 18° C. to that at 0° C. increasing with increasing acid strength.

HCl	1.3	2	2.6	4	8 normal
$R_{18°}/R_{0°}$	1.58	1.68	1.70	2.44	3.25

[1] (*a*) v. Wogan, *Ann. Physik* (4), **23**, 345 (1907); The Svedberg, *Z. physik. Chem.*, **67**, 105 (1909); The and A. A. Svedberg, *Z. physik. Chem.*, **76**, 145 (1911); Öholm, *Medd. Vetens. Akad. Nobel Inst.*, **2**, Nr. 23 (1913).

(*b*) The Svedberg, *loc. cit.*; Öholm, *Medd. Vetens. Akad. Nobel Inst.*, **2**, 24 (1913); **2**, 26 (1913); Dummer, *Z. anorg. Chem.*, **109**, 31 (1919).

(*c*) Scheffer, *Proc. Kon. Akad. Weten. Amsterdam*, **19**, 148 (1916); Cohen and Bruins, *Z. physik. Chem.*, **103**, 404 (1923).

[2] *Ostwald's Klassiker*, No. 104, p. 52.

Spring,[1] investigating the rate of solution of iceland spar in hydrochloric acid, noted that the velocity was dependent on the surface exposed, whether the natural plane of cleavage or a surface parallel to or perpendicular to the principal axis. The temperature coefficient, moreover, was higher in the latter case than with the natural plane of cleavage.

The first theoretical treatment of importance of the problem of reaction velocity at solid-liquid interfaces is due to Noyes and Whitney [2] who chose for study the simple cases of solution in water of the two substances benzoic acid and lead chloride. Cylinders of the substances were rotated rapidly in water, measurements of the solute content being made at definite time intervals from the start. Noyes and Whitney postulated that around the surface of the cylinder a film of saturated solution was continually present and that the solution process was achieved as a result of diffusion of the solute from this layer into the solvent medium. Now, since the rate of diffusion is proportional, according to Fick's Law, to the concentration gradient between the saturated layer and the surrounding solution, it follows that this rate and, consequently that of the solution process, must be determined by the difference in concentration between the saturated layer and the solution. In other words, if S be the concentration of the saturated solution, x that of the bulk of the solution at time t, the rate of solution at time t is given by the equation:

$$\frac{dx}{dt} = C(S - x),$$

where C is the constant of proportionality. It follows that on solving for C

$$C = \frac{1}{t} ln \frac{S}{S - x},$$

which is an equation identical in form with that of a unimolecular reaction. The form of the equation, however, is no index of the order of the reaction, since, as pointed out, it was derived on the assumption that the rate of diffusion determined the total reaction rate. Noyes and Whitney's experimental results gave good confirmation of the correctness of their theory, the mean velocity constants obtained with benzoic acid and with lead chloride being indicated in the following table.

Though irregularities in the value for C for various samples are manifest, the similarity in the results for two such widely divergent substances as benzoic acid and lead chloride was regarded by Noyes and Whitney as full justification of their theoretical treatment.

Brunner and St. Tolloczko [3] amplified the work of Noyes and Whitney, making use of a wider variety of substances, both organic and inorganic, and paying particular attention to the definition of the surface area. More.

[1] *Z. physik. Chem.*, **2**, 13 (1888).
[2] *Z. physik. Chem.*, **23**, 689 (1897).
[3] *Z. physik. Chem.*, **35**, 283 (1900).

TABLE V

VELOCITY CONSTANTS OF SOLUTION PROCESSES

Sample	No. 1	No. 2	No. 3	No. 4
$C_{C_6H_5COOH}$	112.1	163.1	112.7	102.5
	109.1	157.1	117.4	102.8
	107.5	160.1	110.9	94.3
C_{PbCl_2}	71.4	119.0	88.2	56.0
	75.6	125.4	95.2	62.3
	72.7	120.9	86.9	59.2

measurements in each experiment were made and a constant rate of stirring was achieved. These workers observed that, starting with carefully smoothed surfaces of known area, O, the reaction velocity was expressible by the equation

$$k = \frac{1}{Ot}\log \frac{S}{S - x}$$

throughout the experiment, using the initially determined value for O even though its value must have changed owing to uneven erosion of the originally plane surface. This evidence points to the layer of saturated solution as the real interface between the solid and the solution, its effective area being unchanged throughout an experiment. Temperature coefficients of the order of 1.5 to 1.8 per 10° rise were obtained pointing to the predominance of diffusion factors over chemical processes.

Nernst attempted a general theory of reaction velocity in heterogeneous systems [1] based upon the assumption of extremely rapid reaction in the interfacial layer and on slow diffusion of the reactants and resultants from the layer. That this is true in certain cases is evident from the work already recorded and from the experimental work of E. Brunner [2] in Nernst's laboratory and many others. The assumptions, however, are by no means universally valid as subsequent discussion will reveal. Chemical reactions may be slow or fast as compared with the velocity of the diffusion process. Nernst emphasized the factor of the thickness of the interfacial layer in such processes as have already been discussed. Thus, in considering the rate of attack of hydrochloric acid on, for example, magnesia, the quantity of hydrochloric acid dx diffusing in time dt, into a layer of thickness, δ, in contact with an area O, is given by the equation

$$dx = \frac{ODa - x}{\delta V} dt,$$

where D is the diffusion coefficient per unit area per second per unit concentra-

[1] *Z. physik. Chem.*, **47**, 52 (1904).
[2] *Z. physik. Chem.*, **47**, 56 (1904).

tion difference, $\frac{a-x}{V}$ the concentration of hydrochloric acid in the bulk of the solution of volume V. Now since, as shown by Noyes and Whitney,

$$dx = k(a - x)dt,$$

the magnitude k is given by the equation

$$k = \frac{OD}{V\delta};$$

or, in case k is measured, O, D and V known, δ the thickness of the layer can be deduced. Brunner found that the value of k was proportional approximately to the two-thirds power of the frequency of the stirring; the stirring therefore diminished the thickness of the interfacial layer. With a variety of reactions, for example, the rate of solution of benzoic acid in water, of magnesia in benzoic, acetic and hydrochloric acids, of marble in hydrochloric acid and magnesium chloride, of magnesium in benzoic acid and of silver acetate in water, the calculated thickness of the interfacial layer at constant stirring was found to vary only between 20 μ and 50 μ while the velocity of reaction under the same conditions varied as much as 1 : 7. It was found that the rate of reaction bore no relation to the strength of the acid employed. The rate of solution of magnesia in acetic acid is more rapid than the rate in benzoic acid although the latter is the stronger acid. Acetic acid, however, has the higher diffusion rate and hence the greater rate of reaction.

Convincing proof of the applicability of the diffusion layer theory is obtainable from the experiments of Van Name and Edgar[1] on the velocity of interaction of various metals with iodine dissolved in an excess of potassium iodide solution. Mercury, cadmium, zinc, copper and silver were all shown to have practically the same rate of interaction under like conditions, as the following table shows.

With zinc, cadmium and mercury an agreement to within 2 per cent was attained under similar conditions. With copper and silver there are variations up to 5 per cent, attributable in great part to the partial adherence of solid iodide at the interface. The rate of reaction was approximately proportional to the 4/5 power of the stirring velocity. Increase of iodide concentration increased the rate of reaction, an influence ascribed to the higher diffusion velocity of the potassium tri-iodide in stronger potassium iodide solutions, a fact which was demonstrated by qualitative experiment by Van Name and Edgar. A quantitative study of the velocity of diffusion of iodine in potassium iodide solutions was made by Edgar and Diggs.[2] Increase in concentration of the potassium iodide causes a marked increase in the rate of diffusion of the iodine, the amount of increase being distinctly of the same order of magnitude as the increase in the velocity constants, in good accord, therefore, with the

[1] *Z. physik. Chem.*, **73**, 97 (1910).
[2] *J. Am. Chem. Soc.*, **38**, 253 (1916).

TABLE VI

VELOCITY CONSTANTS FOR REACTION BETWEEN IODINE AND VARIOUS METALS

Revolutions per Minute	Concentration of KI in grams per liter			
	100	200	400	800
170	6.43 (Hg) 6.36 (Cd)	7.21 (Hg)	8.15 (Hg) 7.95 (Cu)	
180	7.03 (Zn)		8.23 (Ag)	
210		8.54 (Hg)		
240	8.81 (Hg) 8.69 (Cd) 8.64 (Zn)	9.55 (Hg) 9.56 (Cd) 9.64 (Zn)	10.48 (Hg) 9.98 (Cu) 9.93 (Ag)	10.27 (Cu)
300		11.12 (Hg)		

diffusion theory of heterogeneous reactions. Mercury reacts with bromine in potassium bromide solutions more rapidly than in the iodine solutions; it reacts much more slowly in copper bromide. The ratio of velocities in the three cases is approximately 12.3 : 11.0 : 6.9. It is to be anticipated that bromine would diffuse more rapidly. The low velocity of diffusion of copper salts in comparison with potassium salts is in agreement with the results with copper bromide. Additional studies of the rate of metal-iodine reaction were also carried out by Van Name and Bosworth [1] and by Van Name and Hill.[2] These several researches probably represent the most complete experimental study yet made of a solid-liquid reaction velocity involving the diffusion process as the determinant of reaction rate.

Criticisms of the diffusion theory have been made by Ericson-Auren,[3] Palmaer [4] and Meyer Wildermann [5] in reference to solution processes. The latter claims that the assumption of a diffusion layer is unnecessary since the same velocity equations can be derived without its use. He further shows that the velocity of solution of gypsum is dependent on the physical properties of the material and varies with different faces of the crystal. On a simple diffusion theory, this could not be true. Nevertheless, it should be emphasized that the properties of the diffusion layer will certainly depend in part on the surface exposed, since, as is now well known, adsorption differs at different faces. In Auren and Palmaer's experiments on the velocity of solution of metals in acids, a variety of difficulties might arise. Gas evolution is undoubtedly a complicat-

[1] *Am. J. Sci.*, **32**, 207 (1911).
[2] *Am. J. Sci.*, **36**, 543 (1913).
[3] *Z. anorg. Chem.*, **18**, 83 (1898); **27**, 209 (1901).
[4] *Z. physik. Chem.*, **56**, 689 (1906).
[5] *Z. physik. Chem.*, **66**, 445 (1909).

ing factor in such experiments as some recent work by Prins [1] demonstrates. The velocity of solution of a variety of metals in acids was shown to be markedly influenced by such additions as nitrobenzene and benzaldehyde. Most marked accelerations were noted, especially under such experimental conditions as eliminated or minimized the hydrogen evolution. It is possible that the influence of such additions may be in part catalytic though the mechanism has not been established.

Velocity of Crystallization: That the Noyes-Whitney-Nernst theory of heterogeneous reaction velocity is not adequate for all solid-liquid reaction systems is evident when a study is made of the results of Marc [2] on the velocity of crystallization from aqueous solutions. Marc shows that the process of crystallization is relatively slow and easily measurable; that, in contrast to solution, it is independent of the rate of stirring when this is sufficiently intensive. Foreign substances, adsorbed by the crystal, reduce the rate of crystallization most markedly, which points to the existence of an adsorption layer in which the essential process of crystallization occurs. The existence of this layer is indicated by an initial rapid fall in supersaturation during the first half minute after the crystals have been added to the supersaturated solution, after which time interval a normal crystallization velocity is obtained. The diversity of solution and crystallization phenomena is shown by the observation that the substances which markedly inhibit crystallization do not influence the rate of the solution process. The "order" of reaction varies with the temperature in an unexplained way. At low temperatures (circa 0° C.) the velocity is approximately proportional to the square of the supersaturation; at 25° C., the velocity is "unimolecular." The temperature coefficient of the second order reaction is approximately 1.5, that of the first order reaction approximately 2.0; there is no well-marked change from one to the other order of reaction.

The work of Marc indicated that when a crystal is introduced into a saturated solution there is an initial rapid formation of an adsorption layer; the crystal growth occurs at a measurable rate at the expense of the molecules in this layer which, however, is maintained by further adsorption from the solution. Foreign substances which are adsorbed but which cannot enter the crystal lattice impede the velocity of crystallization, the mechanism of the inhibition being undoubtedly like that of a catalyst poison in heterogeneous catalysis, the diminution of active reaction area as a result of preferential and more or less irreversible adsorption. The accompanying diagram shows the influence of a dissolved dyestuff on the rate of crystallization of potassium sulphate, Curve I showing the uninhibited rate of crystallization, Curve II that with 0.03 g. Quinoline yellow in 100 ccs. of solution. Curve III shows the rate of saturation of an unsaturated solution with potassium sulphate with dyestuff present (points indicated by crosses in circles) and with dyestuff

[1] *Proc. K. Akad. Weten. Amsterdam*, **23**, 1449 (1921).

[2] *Z. physik. Chem.*, **61**, 385 (1908); **67**, 470 (1909); **68**, 104 (1909); **73**, 685 (1910).

absent (circles only). The velocity units are arbitrary and express degree of supersaturation and unsaturation respectively; time is expressed in minutes.

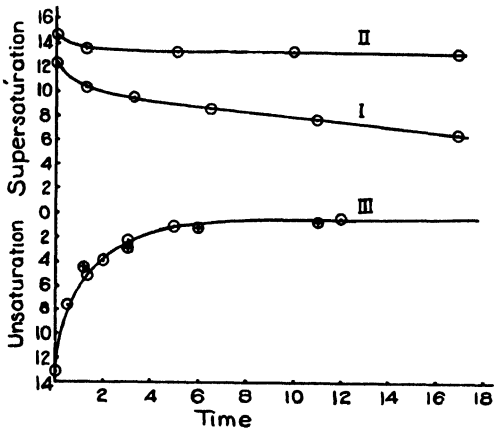


FIG. 1. Velocities of De-Saturation and Saturation of Potassium Sulphate Solutions in Presence and Absence of Dye-Stuffs

That adsorption is an important factor in the process is further evident from the fact that only those dyestuffs which color the crystals inhibit the velocity of crystallization. Bismarck brown, Ponceau red and Quinoline yellow all color potassium sulphate and retard its rate of crystallization. Methylene blue does not color this salt; it exerts no effect on the velocity of crystallization.

Freundlich[1] calls attention to the widespread importance of the subject of crystallization velocity in the presence of foreign substances. The retarding influence of impurities accounts in part for the use of charcoal purification and decolorization of solutions in preparative chemistry. The various crystal formations in living matter, e.g., pearls, probably owe their particular formation to the presence of foreign materials during formation. The multitudinous forms of crystalline configuration of one and the same substance are in part due to this presence of foreign materials. Valeton[2] has discussed the relationship between crystal growth and the lattice structure as determining, for example, the differences between cubic and octahedral crystals of sodium chloride. When crystallized from solutions containing urea, octahedra are formed. Cubic crystals form from the pure solutions.[3] The growth of crystals in colloid media is another phase of the same problem. The influence of foreign substances is not, however, confined to organic substances. Marc showed that substances such as the chloride, nitrate and carbonate of potassium all influenced the velocity of crystallization of potassium sulphate. Some diminished the velocity of crystallization. Potassium chloride doubled the rate.

Crystallization from Melts: The fact that crystals are polyhedra shows that the rate of growth of a crystal differs at different faces. Were this not so, all crystals would be spherical. The earliest work by Gernez[4] on crystallization from a melt is concerned, however, with the so-called linear crystallization velocity. Gernez studied the motion of the visible interface between

[1] Kapillarchemie, 2d Edition, Leipzig, 1922, pp. 457–466.
[2] *Z. Physik.*, **21**, 606 (1920).
[3] Ritzel, *Z. Krist. Miner.*, **49**, 152 (1911); *Z. physik. Chem.*, **76**, 584 (1911).
[4] *Compt. Rend.*, **95**, 1278 (1882).

solid crystal and melt as it extended from the end of a tube through the melt. Gernez employed sulphur and phosphorus and studied the rate of growth of rhombic sulphur and the yellow form of phosphorus. He showed that, with increasing extent of supercooling, the velocity of crystallization steadily rose. Moore [1] showed subsequently that the velocity was independent of the diameter of the tube within the limits of 1 to 7 mm. in the case of supercooled phenol and acetic acid. The subject was studied more comprehensively by Tammann and his students [2] who extended the temperature interval over which the measurements were made. It was found that the velocity was largely a function of the extent of supercooling With slight supercooling, the velocity was extremely slow. With decreasing temperature, the velocity rose until a maximum value was reached which then was maintained more or less constant over a considerable temperature interval, beyond which a decrease in velocity would be observed. The accompanying diagram, Fig. 2, reproduces the general behavior observed. Ordinary glass illustrates a part of this behavior readily. At normal room temperatures, far below the crystallization point, the velocity of crystallization (devitrification) is excessively slow. That it occurs slowly, however, may occasionally be observed in old panes of window glass. Crystal growth is increased in velocity by raising the temperature, a familiar phenomenon to anyone who has experimented much in the art of glass-blowing. Tammann is of the opinion that the form of the curve is determined in large part, not by the velocity of crystallization, but by the rate of heat loss from the system. Since crystallization is an exothermic process, Tammann holds that the heat evolution at the interface exercises a marked influence on the rate of crystallization, by causing the liquid contiguous to the interface to become heated above the melting temperature, thus giving a lower velocity of change than would obtain with true temperature equilibrium. With increased supercooling, this factor becomes less and less important until, in the region of constant velocity, the conditions of heat loss are such that the interface is exactly at the melting temperature. At still lower temperatures, the interface is also lower in temperature than the freezing point. The velocity of crystallization falls, however, as do other reaction velocities with decreasing temperature, and as crystallization would, according to Tammann, even at low degrees of supercooling, were the other factors not simultaneously operating in the less supercooled fluids.

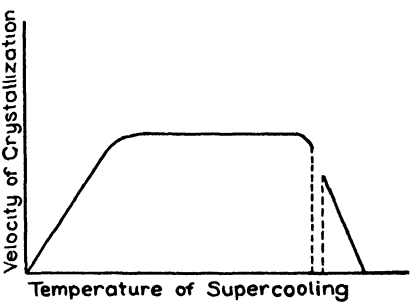


FIG. 2. Velocity of Crystallization from Melts

In Table VII are indicated some measurements of the maximum linear velocity of crystallization in a few supercooled fluids, which show a wide

[1] *Z. physik. Chem.*, **12**, 545 (1893).

[2] Kristallisieren und Schmelzen, Leipzig, 1903, pp. 131 et seq.

variation of this magnitude. No relationship is known connecting this velocity with the properties of the various substances. A wide variation is, however, observable.

TABLE VII

MAXIMUM VELOCITIES OF CRYSTALLIZATION

Substance	M. P. ° C.	Bath Temp.	Velocity mm. min.	Observer
Phosphorus	44°	25°	60000	Gernez
Water	0	− 9.1	6840	Walton and Judd [1]
Butylphenol	98.1	70	1117	Jendrychowski [2]
Picric Acid	122	85	858	Bogojawlensky [3]
Azobenzol	67.1	37	600	Friedlander and Tammann [2]
Benzil	94.8	60	433	Bogojawlensky [2]
m-Dinitrobenzoic Acid	140	120	31	Bogojawlensky [2]
Salol I	42	20	3.46	Tammann [2]
Salol II	38.8	20	1	Tammann [2]

These measurements relate to linear velocity of crystallization, which certainly is a composite quantity. A determination of true velocity of growth of individual crystal faces has finally been realized by Nacken [4] whose researches on the subject throw some doubts on Tammann's interpretation of the previous diagram. Nacken observed microscopically the crystallization of crystals growing under cover glasses and was able to notice very diverse rates of growth at various faces, varying from one another relatively greatly with temperature. Furthermore, by regulating the temperature loss or gain to crystals attached to metals he was able to maintain any temperature of crystal desired. In this way he showed it to be possible to regulate the form of the growing crystal. As long as the heat of crystallization was greater than that of heat loss, the melting point temperature was maintained at the interface and hemispherical or ellipsoidal solids were formed, the former from crystals of the regular series, the latter from other crystal systems. If the heat loss is greater, however, than the heat of crystallization, crystallization starts first at the surfaces with the smallest velocity of crystallization, with formation of a surface on the rounded solid. With the heat loss somewhat greater, crystallization starts at surfaces having greater velocities of crystallization. If Tammann's theory were correct, these phenomena should only be observable at temperatures at which the maximum linear velocities obtain. For, only at such temperatures, according to Tammann, does the melting temperature prevail at the crystal surface. Nacken showed however that this formation of crystal faces commences for Salol (cf. Table VII) some 1° or 2° below the melting point. Nacken

[1] *J. Phys. Chem.*, 18, 722 (1914).

[2] Cited from Kristallisieren u-Schmelzen, pp. 146–147.

[3] *Z. physik. Chem.*, 27, 585 (1898).

[4] *Zentralbl. f. Min. Geol. u. Pal.*, 191 (1917). *Neues Jahrbuch f. Min. Geol. u. Pal.*, 2, 133 (1915).

such work, attention must be directed to an analysis of the temperature influence on the individual steps of the composite process which the determination of reaction velocity measures. Thus, while experiment should undoubtedly be directed to a test of Denham's views, it should simultaneously be ascertained what is the effect of temperature on the extent of adsorption by colloidal and by massive materials. The data available to give even an orientation in such a question are most scanty. If, however, the decrease in amount adsorbed with a given temperature rise is very much more pronounced in the case of a massive, poorly adsorbing surface than with a colloidal surface, this would result in a lower temperature coefficient for the reaction at a massive surface. It is probable that this somewhat difficult problem will be more easily approached by a study of gaseous adsorption at catalytic surfaces since, under such conditions, experimental procedure would be simplified. Such data must be accumulated before satisfactory elucidation of the problem of temperature coefficient in catalyzed reactions in solid-liquid systems can be obtained.

It is necessary in concluding this general survey of catalyzed reactions at solid-liquid interfaces to add some observations concerning the nature of the concentration of reactants at the interface. The modern point of view in this regard is gravitating to a position midway between two extreme viewpoints which were earlier held. Starting with the observations of Faraday [1] on the power of metals to adsorb gases and to compress and concentrate gases by such adsorptive power, the one school has viewed the mechanism of concentration at the interface as due to a purely physical force of adsorption. Chemical action was supposedly enormously accelerated by such compression and concentration, the contact agent or catalyst playing a very subordinate, if not negligible, rôle. This point of view was dominant in the researches of van't Hoff [2] on the decomposition of gases at the surfaces of the containing vessel. It finds expression in numerous researches by a variety of capable investigators, among whom may be mentioned Bredig and Findlay,[3] J. J. Thomson,[4] Spring,[5] Bodenstein,[6] Euler,[7] Henri,[8] Bayliss,[9] and Denham.[10] Bancroft [11] has recently summarized the material relative to the adsorption viewpoint.

Side by side with this physical concept, the chemical view of definite though unstable intermediate compounds has received much consideration and support. It was first put forward by de la Rive and Marcet [12] and has since that time received continued support in various directions. Their concept of an inter-

[1] Experimental Researches in Electricity, 1849, **1**, 165, 6th series. Nos. 564–659.
[2] Physico-Chemical Studies, Vol. I (1898).
[3] Anorganische Fermente, p. 92.
[4] Applications of Dynamical Statics, pp. 206, 236.
[5] *Bull. Acad. Belge*, (3) **30**, 27.
[6] *Z. physik. Chem.*, **60**, 1 (1907).
[7] *Ofvers. Svensk Akad. Forhand.*, 267 (1900).
[8] *Z. Elektrochem.*, **11**, 790 (1905).
[9] Nature of Enzyme Action, p. 14 (1908).
[10] *Z. physik. Chem.*, **72**, 684 (1910).
[11] *J. Phys. Chem.*, **21**, 767 (1917); *Trans. Am. Electrochem. Soc.*, **37**, 31 (1920).
[12] *Ann. Chim. Phys.*, (2) **39**, 328 (1828).

mediate platinum oxide as a stage in catalytic oxidation was extended by Berthelot [1] to hydrogen peroxide decomposition. Haber [2] re-emphasized this view and Bredig, from his researches on the catalytic activity of colloidal platinosols, concluded that this was the most convenient explanatory assumption. Bredig and von Antropoff [3] actually revealed the intermediate formation of mercuric peroxide in the decomposition of hydrogen peroxide at a mercury surface, the mercury peroxide forming a film which then breaks down, only to form again. This peroxide phenomenon represents an extreme case. Under ordinary circumstances the formation and decomposition succeed one another extremely rapidly and are impossible of detection. Intermediate peroxide formation may account in some cases for the similar activity of various oxides as catalysts for hydrogen peroxide decomposition. In other cases as, for example, at powdered glass and quartz surfaces, such peroxides are not easily assumed and in such cases adsorption is suggested. Sabatier [4] expounded the point of view of intermediate compound formation in reference to catalytic hydrogenation of organic compounds at metal-liquid and metal-gas interfaces, reasoning from the capacity displayed by the platinum metals to absorb hydrogen, with the possible production even of hydrides. In his view, hydrogenation is carried on by double decomposition between the metal hydride and the unsaturated organic compound. Armstrong and Hilditch [5] have supplemented Sabatier's idea relative to a metal-hydrogen association by emphasizing the primary importance of the metal-organic compound association. Their researches, which will be detailed at length in the subsequent examples, demonstrate that hydrogenation at the surface of a catalyst is explained by primary interaction between catalyst and unsaturated compound (an action produced by chemical forces, but not necessarily giving a stable isolable compound), the complex so formed being decomposed by hydrogen. The hydrogen is also to be regarded as coupled with the nickel used as catalyst, both hydrogen and unsaturated compound being considered as having some affinity for the nickel.

The newer work on adsorption at surfaces is supplying the necessary material which will enable such extreme points of view to be brought together. The field of adsorption ranges between these two extremes. At one time thought to be practically purely physical and non-specific, adsorption is now being shown to be composite of varied phenomena, many of which are extremely specific and akin to purely chemical phenomena. Langmuir's researches [6] on the behavior of oils spread in unimolecular layers [7] on water surfaces are evidence in favor of the view that molecules may be held to a

[1] *Ann. Chim. Phys.*, (V) **21**, 176 (1880).

[2] *Z. anorg. Chem.*, **18**, 39 (1898); *Z. physik. Chem.*, **34**, 575 (1900).

[3] *Z. Elektrochem.*, **12**, 581 (1906); *J. prakt. Chem.*, (2) **77**, 273 (1908).

[4] Catalysis in Organic Chemistry, Sabatier-Reid, pp. 51–53. D. van Nostrand Co. (1922).

[5] *Proc. Roy. Soc*, 1919–1923.

[6] *J. Am. Chem. Soc.*, **38**, 2221 (1916); **39**, 1848 (1917); **40**, 1361 (1918).

[7] Rayleigh, *Proc. Roy. Soc.*, **47**, 364 (1890). Hardy, *Proc. Roy. Soc.*, **86A**, 631 (1912); **88A**, 303 (1913).

surface by forces which are not readily distinguishable in effect from "chemical" forces or affinity. It is such molecules at the contact surface which enter into catalytic changes. It is undoubtedly true, however, that not all adsorption at a contact surface leads to catalytic change. Specificity on the part of the contact agent is still a striking factor which must be remembered. Copper is a useful agent for the hydrogenation of ethylenic compounds but is not used for the hydrogenation of the aromatic nucleus, although it undoubtedly adsorbs benzene and its derivatives. Similarly, carbon monoxide is adsorbed by copper but is not hydrogenated in its presence. This diversity of behavior will undoubtedly be accounted for by a more penetrating analysis of the nature of the association between catalyst and reactant, with a view to distinguishing the extent of intra-molecular change suffered by reason of the association. In the meantime, the tendency of catalyst and reactant to form compounds is a rough index of such intra-molecular change. Langmuir's work has already revealed that the adsorptive force, chemical in nature, determines the orientation of molecules at the interface between two liquids, and the concept of orientation is definitely transferable to solid-liquid and solid-gas interfaces. This molecular orientation undoubtedly accounts in part for the efficacy or otherwise of a contact agent in promoting change, as the experiments of Kruyt and van Duin [1] reveal. They find that the following reactions are retarded by charcoal although the reacting substances are adsorbed by it: the saponification of ethyl acetate and of sodium methyl benzoate *p*-sulphonate; the addition of bromine to the acid sodium salt of *p*-sulfo-cinnamic acid; the removal of bromine from the neutral and the acid sodium salts of *p*-sulphonic dibromohydro cinnamic acid by means of potassium iodide. On the other hand, the removal of bromine from $\alpha\beta$-dibromopropionic acid by means of potassium iodide is accelerated by the presence of charcoal. In this latter case there are three polar groupings, Br, Br, COOH, in the acid and, according to the theory of oriented adsorption, the chain of carbon atoms takes up a position parallel to the boundary carbon surface with the three polar groups turned to the water, in a favorable orientation for reaction. In the other cases, unfavorable orientations result. Such examples must be multiplied by further experimental test.

Exemplification of the many points raised in the general discussion of these catalytic processes at solid-liquid interfaces may now be given.

Apparent Zero Order Reactions: Among the most convincing studies of the reactions occurring at rates independent of the concentration of the reacting species (Case I of the previous discussion) are those of Armstrong [2] on the rate of hydrolysis of sugars in presence of enzymes. The following table shows the results with concentrated solutions of milk sugar and lactose in which the amount of enzyme present was quite small. It will be seen that the absolute amount of sugar hydrolyzed is independent of the concentration within a wide

[1] *Rec. Trav. Chim.*, (4) **2**, 249 (1921).
[2] *Proc. Roy. Soc.*, **73**, 500 (1904).

limit of variation. The reaction velocity equation is therefore of the form

$$\frac{dx}{dt} = kS,$$

where S is the sugar concentrated at the surface of the enzyme and which, under the stated experimental conditions, is apparently constant.

TABLE VIII

HYDROLYSIS OF CONCENTRATED SUGAR SOLUTIONS

Concentration of Sugar Solution Per Cent	24 Hours		46 Hours		144 Hours	
	Amount Hydrolyzed Per Cent	Absolute Amount Hydrolyzed g.	Amount Hydrolyzed Per Cent	Absolute Amount Hydrolyzed g.	Amount Hydrolyzed Per Cent	Absolute Amount Hydrolyzed g.
10	14.2	1.42	22.2	2.22	33.4	3.34
20	7.0	1.40	10.9	2.18	16.9	3.38
30	4.8	1.44	7.7	2.21	11.0	3.30

When the ratio of enzyme present to sugar was relatively high, the above conditions no longer held and the following table shows that, on increasing the amount of sugar present, there was a nearly proportionate increase in the amount hydrolyzed, though the proportion hydrolyzed as well as the constant K for a unimolecular reaction (Case II previously) remained constant.

TABLE IX

DILUTE SUGAR SOLUTIONS

Milk Sugar per 100 cc.	Amount changed in 3 hours	K (Unimol.)
1.0 g.	0.185	0.0296
0.5 g.	0.098	0.0298
0.2 g.	0.0416	0.0337

In the most dilute solution a marked rise in K is to be noted. This evidently is to be ascribed to the operation of the factors enumerated in Case III. Experiments on the influence of enzyme concentration showed that the hydrolysis was approximately proportional to the amount of enzyme, provided that the amount was not too large and that the comparison was made during the earlier stages of the hydrolysis. This is the result to be expected on the basis of a surface effect when it is remembered that the reaction products do eventually exert a marked influence on the rate of reaction. Similar results to those obtained by Armstrong have been obtained by Hudson [1] with cane

[1] *J. Am Chem. Soc.*, **30**, 1160, 1564 (1908).

sugar and invertase and by Nelson and his coworkers in the studies previously cited.

In the realm of solid-liquid interface reactions at metallic surfaces, the studies of Armstrong and Hilditch [1] on the rate of hydrogenation of unsaturated compounds at the surface of a nickel catalyst are both comprehensive and convincing. Several workers, such as Fokin,[2] Moore, Richter and van Arsdel,[3] Ueno,[4] Ubblehode and Svanoe [5] and Thomas,[6] have observed an approximation to a unimolecular action in hydrogenation of liquid systems at a nickel surface. Employing as pure materials as could possibly be obtained and working under mechanical conditions favoring maximum contact of the gaseous, liquid and solid components of the system, Armstrong and Hilditch found that unsaturated glycerides containing mixtures of olein and less saturated glycerides gave characteristic curves, more nearly a series of two straight lines than a combination of two unimolecular curves. The first (almost linear) segment corresponded to the portion of the process in which analysis of the product has shown that the main action is the transformation of less saturated glycerides to olein and the second portion (not so straight) covers the part of the action in which olein (with the iso-oleins also formed in this action) is passing to stearin.

Later, Armstrong and Hilditch extended the study to suitable unsaturated organic individuals which could be obtained in a state of greater purity than the non-volatile glycerides. The linear character of the absorption of hydrogen-time curves became very definite. It was also shown how the linear curves could be transformed into unimolecular curves (i) by the presence of a substance which slowly combines with the catalyst to form a permanent compound (permanent catalyst poisoning) or (ii) by the accumulation of gaseous impurities in the gas-space above the acting system (thereby altering the otherwise constant concentration of hydrogen above the liquid). A further possibility resulting from this latter effect is that such gaseous impurities may have been *preferentially* adsorbed by the nickel catalyst and thus exercised a retarding influence on the reaction more than proportionate to their actual concentration in the gas phase. The linear curves obtained by Armstrong and Hilditch in these studies undoubtedly indicate that the chosen experimental conditions gave a catalyst surface which was, initially and for a prolonged period of time, completely saturated with reactants. The deviations from linearity in the later stages of the reaction are also to be ascribed in part to competition of reaction products for the nickel surface, since it has been shown [7] that even saturated hydrocarbon systems, e.g., ethane, cyclohexane, are strongly adsorbed by catalytic metals.

[1] *Proc. Roy. Soc.*, **96A**, 137 (1919); **98A**, 27 (1920); **100A**, 240 (1921).

[2] *Z. angew. Chem.*, **22**, 1451, 1492 (1908).

[3] *J. Ind. Eng. Chem.*, **9**, 451 (1917).

[4] *J. Chem. Ind. Tokio*, **21**, 749 (1918).

[5] *Z. angew. Chem.*, **32**, 257, 276 (1919).

[6] *J. Soc. Chem. Ind.*, **39**, 120 (1920).

[7] Pease, *J. Am. Chem. Soc.*, **45**, 1196 (1923). Dougherty and Taylor, *J. Phys. Chem.*, **27**, 533 (1923).

Throughout the preceding work the operating pressure of hydrogen gas was maintained constant. In a subsequent contribution, Armstrong and Hilditch[1] discussed the influence of variation in the hydrogen pressure. In this investigation, the greater complexity of the bimolecular reaction at an interface reveals itself quite definitely.

(i) Normal: In the absence of substituent groups of the kind discussed below, (iii), and in presence of sufficient nickel (in general, so long as at least 0.1 per cent of nickel is present) the ethylenic union is hydrogenated at a rate which is in almost exact proportion to the absolute pressure of the hydrogen.

(ii) Subnormal: At very low concentrations of catalyst (say 0.01 to 0.02 per cent of nickel reckoned on the organic compound) the increase in rate of hydrogenation becomes less than proportional to the increase in pressure. The compounds which absorb hydrogen most readily are in general more prone to show this subnormal effect when the catalyst concentration is diminished and it is especially marked in the case of multi-ethylenic compounds such as derivatives of linoleic acid or linolenic acid or with citral.

(iii) Abnormal: If the unsaturated compound contains another group which has affinity towards nickel (but is not open to hydrogenation), it is found that increase in hydrogen pressure causes an increase in the rate of hydrogen adsorption in more than simple proportion to the altered concentration of hydrogen. This has been observed with unsaturated alcohols and unsaturated carboxylic acids. Unsaturated aldehydes or ketones on the other hand show normal or subnormal behavior.

The results are broadly, then, that increase in concentration of hydrogen causes a directly proportionate increase in the rate of hydrogenation providing there are no disturbing factors; and that the increase in rate of hydrogenation becomes abnormally large if other groups active towards nickel but not open to hydrogenation are present. In other words, the nature of the organic compound has a determining influence on the effect of hydrogen concentration.

By analogy with results of Pease, subsequently to be discussed (p. 989), on the mechanism of hydrogenation of ethylene at a gas-solid interface, the proportionality between rate and pressure in the normal case is to be ascribed to the fact that the extent of association between nickel and organic compound is large as compared with that between nickel and hydrogen. The accessibility of the hydrogen to *free* nickel surface (which will be small) varies directly as the hydrogen pressure. In the subnormal cases it is apparent also that the low concentration of nickel means a still lower accessibility of hydrogen to *free* nickel surface, the reduction in catalyst quantity being less unfavorable to the more strongly associated reactant, the unsaturated body. In the case of abnormal variation with pressure, the abnormality apparently lies in the secondary association of nickel with the unsaturated body at the second group which is not subject to hydrogenation. If it be assumed that this is a position of stronger association with nickel than the unsaturated linkage which can be hydrogenated, it follows that the influence of increased hydrogen pressure will

[1] *Proc. Roy. Soc.*, **100A**, 240 (1921).

be greater than in the case where only one type of association between nickel and unsaturated body is possible. It will need careful and painstaking research to verify such a point of view quantitatively. The work of Langmuir and Hardy previously cited is a beginning in that direction. Progress, however, may come more rapidly by the study of mechanism in vapor phase hydrogenation reactions, where, as Pease has shown, it is possible more easily to follow the variation of interfacial concentration.

The temperature coefficient of such hydrogenation processes may be judged from the curves given in Fig. 3. Actual calculation gives a temperature coefficient of 1.2 per 10° rise in the case shown. In view of what has preceded, it is evident that this temperature coefficient is composite of the influence of temperature on (*a*) the velocity of the chemical reaction, (*b*) the extent of complex formation between nickel and unsaturated organic compound, and (*c*) the association between nickel and hydrogen. Of these, the first doubtless increases with the temperature, the two last, on the contrary, undoubtedly decrease.

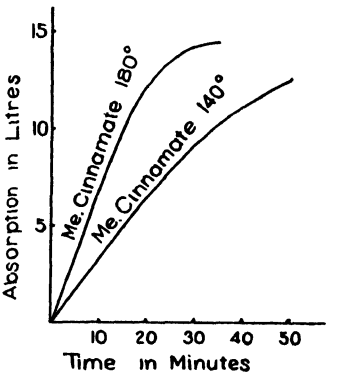


FIG. 3. Variation of Reaction Rate with Temperature

Pseudo-Unimolecular Reactions: A wide variety of catalytic reactions at solid-liquid interfaces conform to the unimolecular velocity equation, Case II of the preceding discussion. The decomposition of hydrogen peroxide solutions is perhaps the oldest and most often studied. This reaction was used by Bredig in conjunction with Muller von Berneck and Ikeda [1] to demonstrate the analogy existing between ferments and colloidal metals, such as platinum, prepared by the Bredig method of passing an arc between two pieces of the metal under water. Bredig and von Berneck showed that such colloidal platinum behaved similarly to platinum black but far more efficiently. It was shown that it was possible to study the kinetics of the reactions quantitatively and to obtain reproducible results. Platinum in a dilution of 1 gram atom of metal in 70 million liters was found to have a marked accelerating action. In alkaline media, one mol. MnO_2 in 10 million, Co_2O_3 in 2 million, CuO in 1 million and PbO_2 in 1000 liters of water had marked catalytic properties. In acid solutions, the effectiveness of these oxides was less. With constant amount and condition of the platinum colloid the decomposition was shown to give good unimolecular constants.

In alkaline media, on the other hand, some results indicated a reaction velocity of the zero order,

$$-\frac{dC}{dt} = k,$$

[1] *Z. physik. Chem.*, **31**, 258 (1899); **37**, 1 (1901).

TABLE X

$\frac{1}{31,500}$ Pt, 36 Days old; $\frac{1}{2000}$ Na_2HPO_4; $\frac{1}{48}$ H_2O_2

Time in Mins.	$a - x$	$k_{unl.}$
0	22.0	—
10	17.2	0.0107
20	13.5	0.0106
30	10.6	0.0106
40	8.2	0.0107
50	6.5	0.0106

similar to those already discussed in the preceding section. This only held, however, in special cases and was not general. It was found that the reaction velocity increased rapidly, with increasing concentration of sodium hydroxide, to a maximum at approximately 0.03*N*. NaOH, beyond which the velocity was rapidly diminished until, in 1*N*. NaOH, it was slower than in water solution. It may be observed that such behavior was also found by Jacobson [1] in the study of hydrogen peroxide decomposition by organic ferments in presence of varying proportions of alkali. The most striking parallelism between the colloidal metal and ferments was found in the "poisoning" action of a wide variety of substances. These "poisons" were studied intensively by Bredig and Ikeda in the second of the researches cited above. The various poisoning actions were attributed to one or other of four causes, the principal cause being, as is now well known, the change in surface and adsorption capacity of the colloidal surface for hydrogen peroxide owing to preferential adsorption of the "poisons". The bearing of these conclusions on much of the preceding work was fully dealt with in these two comprehensive monographs.

In a subsequent study of hydrogen peroxide decomposition at massive platinized platinum surface, Bredig, in conjunction with Teletow,[2] attempted to demonstrate that the reaction was comparable with the studies of Nernst-Brunner on the velocity of solution, namely, that the reaction measured was essentially a diffusion process. The reaction was shown to be apparently unimolecular, the constant of which, at constant rates of stirring, was inversely proportional to the volume of the solution containing unit quantity of hydrogen peroxide. Thus, the following table shows the unimolecular constants obtained for various dilutions at approximately constant rates of stirring.

TABLE XI

Rate of Stirring Revs. per Min.	Volume in Ccs.	$K_{unl.}$
255	450	.0067
235	450	.0060
245	675	.0046
250	1350	.0020

[1] *Z. physiolog. Chem.*, **16**, 349.

[2] *Z. Elektrochem.*, **12**, 581 (1903).

The rate varied as the 2/3 power of the stirring rate. It was concluded that it was not the actual surface, but the "Brunner-quadratic surface," namely, the diffusion layer, which determined the reaction speed.

Senter [1] studied the kinetics of the decomposition of hydrogen peroxide solutions catalytically accelerated by the enzyme hæmase in blood. He showed that in sufficiently dilute solutions a constant, unimolecular with respect to the peroxide and directly proportional to the enzyme concentration, was obtained.

$$-\frac{dC_{H_2O_2}}{dt} = kC_{H_2O_2} \times C_{\text{Enzyme}}$$

The reaction was found to go relatively more rapidly, however, in the more dilute solutions, which fact points to the operation of factors of the type discussed in Case III previously. The temperature coefficient is 1.5 per 10° rise. It was shown in the second communication that a wide variety of substances inhibited the decomposition in a manner entirely analogous to that observed by Bredig and Ikeda with colloidal platinum. The parallelism as to "poisoning" action was not absolute, however. Some specificity of the two adsorbents is manifest in comparing results. Senter, in a succeeding communication,[2] suggests that the Nernst theory of heterogeneous reactions is the plausible explanation of the reaction velocity results.

A more recent study of the peroxide decomposition by Elissafoff [3] provides very definite proof that, at least in some cases, the catalytic activity is determined by the quantity of peroxide adsorbed. Elissafoff studied the action of glass wool and heavy metal salts on the velocity of decomposition, both singly and in conjunction with each other. Elissafoff showed that, together, the glass wool and heavy metal salt effected a much more rapid decomposition of the peroxide than would be anticipated on the basis of additive effects. Thus, with a decomposition velocity of 0.86 in presence of 0.5 g. glass wool in 20 ccs. of peroxide, and one of 1.63 in presence of a 1.54 millimolar solution of copper sulphate without glass wool, a solution with the same copper sulphate concentration plus 0.5 g. glass wool in 20 ccs. gave a decomposition velocity of 10.8; all the velocities are expressed in arbitrary units. The concentration of hydrogen peroxide was 12 millimolar. This phenomenon, which the student of catalysis terms "promoter action," is quite frequently encountered [4] but has been little understood. In this case, at least, the mechanism is apparent. It is known that the decomposition of peroxide takes place at the glass surfaces. It is probable that the copper salt is concentrated at the glass surface and so exercises greater effect. That this is so, the following observations indicate clearly. The unimolecular constants for two copper ion concentrations of 1 and 10 millimols per liter were 0.0013 and 0.0023 respectively,

[1] *Z. physik. Chem.*, **44**, 257 (1903); **51**, 673 (1905).

[2] *Z. physik. Chem.*, **52**, 737 (1905).

[3] *Z. Elektrochem.*, **21**, 352 (1915).

[4] See Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

in the ratio, therefore, of 1 : 1.77. The amounts of copper salt adsorbed from these solutions by Jena glass powder of the same glass were in the ratio of 1 : 1.73. It is apparent that the decomposition velocities are proportional to the amounts of adsorbed copper salt. The velocity measured in this case is certainly therefore a reaction velocity at the surface and not a diffusion velocity. Were it possible to make adsorption measurements, other modes of decomposition of hydrogen peroxide would doubtless be found to be of the same type.

Several catalytic oxidation processes at solid-liquid interfaces apparently obey the unimolecular reaction velocity equation. Ernst [1] showed that the combination of hydrogen-oxygen mixtures in stoichiometric proportions at the surface of colloidal platinum suspended in water was directly proportional to the amount of colloid and to the total gas concentration. An excess of one or other gas apparently behaved as a diluent. Numerous researches have indicated the catalytic influence of platinum surfaces in oxidation-reduction phenomena. Jablczynski [2] noted the oxidation of chromous to chromic salts in presence of acids:

$$\ddot{Cr} + H^{\cdot} = \dddot{Cr} + H.$$

Chilesotti [3] noted the reducing effect of hydrogen on molybdic acid in presence of platinum; Manchot and Herzog [4] recorded the accelerating action of platinum on the reaction,

$$(Co(CN)_6)'''' + H^{\cdot} = (Co(CN)_6)''' + H.$$

Oberer [5] observed increased oxygen evolution from a solution of cobaltic sulphate when a piece of platinized platinum was inserted in the solution. Baur and Glässner [6] noted slight evolution of oxygen when ceric salts were similarly treated. Spencer and Abegg [7] showed the oxidation of thallous ion to occur at an anodically polarized platinized platinum electrode. Diethelm [8] observed the catalytic oxidation at a platinum surface of trivalent titanium to the tetravalent stage. This latter reaction was studied in detail by Denham [9]; it is probably typical of a large class of such oxidation reduction changes. Denham showed that the reaction

$$Ti^{III} + H^{\cdot} = Ti^{IV} + H$$

is catalyzed in both directions by platinum surfaces and that the reaction is pseudo-unimolecular. At a constant acid concentration, a definite equilibrium is reached. The temperature coefficient of the reaction at the platinized platinum surface was 1.29 per 10° rise, indicating a diffusion velocity. Temper-

[1] *Z. physik. Chem.*, **37**, 448 (1901). See also, Hofmann, *Ber.*, **49**, 2369 (1916); **53**, 298 (1920) **55**, 273 (1922).

[2] *Z. physik. Chem.*, **64**, 748 (1908).

[3] *Z. Elektrochem.*, **12**, 146 (1906).

[4] *Ber.*, **33**, 1742 (1900).

[5] Diss. Zurich (1903).

[6] *Z. Elektrochem.*, **9**, 534 (1903).

[7] *Z. anorg. Chem.*, **44**, 379 (1905).

[8] *Z. physik. Chem.*, **62**, 129 (1908).

[9] *Z. physik. Chem.*, **72**, 641 (1910).

ature displaced the equilibrium towards the Ti^{IV} side. The reaction velocity was independent of the hydrogen pressure between 76 cm. and 10 cm. mercury pressure.[1] The velocity of the reaction was, within experimental error, the same with the chlorides as with the sulphates. The equilibrium positions in the two cases were markedly different. The reaction appears to be a suitable one with which to perform experimental work on adsorption with a view to deciding definitely whether the velocity measured is a diffusion velocity or that of a chemical reaction.

Reaction Velocities Conforming to Case III: In several of the reactions discussed in the two preceding sections there is evidence that the proportionality between concentration of solution and that at the interface is determined, over a portion of the concentration range, by the adsorption isotherm equation of Freundlich,

$$\alpha = kc^{1/n},$$

whence a velocity equation of the form

$$-\frac{dc}{dt} = kc^{1/n}$$

may be deduced. This equation is likewise applicable to the decomposition of formic acid solutions at a surface of rhodium, studied by Blackadder.[2] In its integrated form, the expression becomes:

$$k = \frac{1}{1 - \frac{1}{n}t}(C_0^{1-1/n} - C_1^{1-1/n}).$$

Special conditions are necessary before the equation holds. Weak acid concentration is necessary so that addition of sodium formate favors the reaction. The sodium salt does not increase the adsorption of the formic acid. In alkaline media no decomposition occurs. It follows from this that the velocity of decomposition must show a maximum in weakly acid solution. The presence of oxygen or sulphur apparently favors the decomposition, since one or other of these substances must be present. Presumably these elements form the surface of the catalyst and the formic acid is adsorbed on them. The temperature coefficient of the reaction is 2, which indicates that a chemical reaction velocity is being measured, with little temperature influence on the concentration of adsorbate.

The decomposition of sodium hypophosphite at a surface of palladium sponge

$$NaH_2PO_2 + H_2O = NaH_2PO_3 + H_2$$

[1] See Pollard, *J. Phys. Chem.*, **27**, 365 (1923). The adsorption of hydrogen gas by platinum is independent of the partial pressure of hydrogen in approximately this pressure range at 0° C.

[2] *Z. physik. Chem.*, **81**, 385 (1912).

is a reaction which, according to Sieverts and Peters,[1] conforms to the equation given above. It also shows a high temperature coefficient, 2 for a 10° rise. The velocity is directly proportional to the amount of palladium used.

REACTION VELOCITIES IN LIQUID–LIQUID SYSTEMS

Kinetic studies of reactions occurring in systems composed of two liquids or solutions are comparatively few. They are none the less of interest theoretically and of very considerable importance in applied chemistry. The velocity factor is employed in all extraction processes making use of solvents for the concentration of a desired product from a dilute solution; it is the fundamental factor in the hydrolytic processes of the soap and candle industries; in nitration, sulphonation and many other operations of the organic chemist, in the laboratory and in industry, the velocity of reaction in liquid-liquid systems is of first importance in determining the relation between time of operation and working conditions. The problem in this case is somewhat more complex than that just treated in the case of solid-liquid systems. In the latter, reaction is confined by the nature of the solid phase mainly to the interface between the two phases. In liquid-liquid systems, where mutual solubility and solution of other reactants in the two liquids may occur, the kinetic study may extend beyond the interface into the two solutions. The net result in such case may be due to a multiplicity of individual reactions each with their own characteristic and independent kinetic properties.

The Velocity of Mutual Solubility of Liquids and of Distribution between Two Liquids: No considerable body of experimental evidence exists as to these two factors which are both of importance in extraction processes. It is known, however, that both processes are rapid, probably too rapid to be readily measured and dependent in large degree on the efficiency with which the two phases are brought into intimacy of contact by mechanical means. Berthelot and Jungfleisch [2] in experiments on the distribution of bromine and iodine between water and carbon disulphide suggested that equilibrium was attained in a few hours. Nernst,[3] on the other hand, denies this, expressing his "astonishment at the rapidity and certainty with which the equilibrium state was reached."

Reaction Velocity in One Liquid Phase Only: The simplest case of reaction velocity in liquid-liquid systems is that in which the reaction occurs in one liquid phase only or in which the velocity in the second phase is negligibly small. A case of this type is the rate of hydrolysis of an ester in aqueous solution when the ester is only partially miscible with water and is present in excess. Such a case was studied by Lowenherz.[4] In this case, the reaction in the ester phase is negligible as compared with that in the water phase more especially if the latter contain a catalytic accelerant. With excess of the ester

[1] *Z. physik. Chem.*, **91**, 199 (1916).
[2] *Ann. Chim. Phys.*, (4) **26**, 396, 408 (1872).
[3] *Z. physik. Chem.*, **8**, 119 (1891).
[4] *Z. physik. Chem.*, **15**, 3.9 (1894).

and therefore a constant concentration of ester, namely, the saturation concentration, in the aqueous layer, the reaction velocity equation becomes

$$\frac{dx}{dt} = kC_{\text{ester}}C_{\text{cat.}},$$

where $C_{\text{cat.}}$ is the concentration of catalyst. If the latter is an acid and therefore unchanged in concentration throughout the reaction process, the equation becomes quite simply

$$dx/dt = K.$$

A constant amount of ester is changed per unit of time. With alkaline hydrolysis, in which the concentration of alkali is constantly diminishing as a result of reaction, the equation becomes

$$dx/dt = KC_{\text{alkali}}.^{1}$$

The equation is, therefore, in this case, unimolecular in form. These two cases represent the main velocity considerations in the hydrolytic splitting of fats by strong acids and by bases in the soap and candle industries.

A case studied by Goldschmidt and Messerschmidt [2] represents a more complicated case of the same type. They studied the hydrolysis of an ester distributed between an aqueous acid solution and benzene. They assumed the distribution of the solutes between the two phases to be very rapid and neglected the possibility of a measurable reaction rate in the benzene phase. Let a represent the absolute amount of ester, V_1 and V_2 the volumes of the aqueous and benzene layers respectively. At time t let b be the amount of ester in the water layer, x the amount hydrolyzed. Let the distribution coefficient of the ester be C and therefore equal to

$$\frac{b}{V_1} \times \frac{V_2}{a - b - x} = C.$$

Hence,

$$b = \frac{V_1C}{V_2 + V_1C}(a - x).$$

The differential equation thus becomes

$$\frac{dx}{dt} = kb = k\frac{V_1C}{V_2 + V_1C}(a - x),$$

which, on integration, gives

$$k = \frac{1}{t}\frac{V_2 + V_1C}{V_1C}\log\frac{a}{a - x}$$

[1] As a first approximation. See preceding chapter for detailed discussion of the factors in saponification in homogeneous media.

[2] *Z. physik. Chem.*, **31**, 235 (1899).

or for the case $V_1 = V_2$

$$k = \frac{1}{t}\frac{1+C}{C}\log\frac{a}{a-x}.$$

It is easily seen that the reaction in this case must go more slowly in heterogeneous system than in homogeneous system, more slowly the smaller the value of C, or the less the ester concentration in the aqueous layer. This provides a convenient method for slowing down a reaction which proceeds rapidly in a given medium. It is only necessary to add a large volume of a second solvent, immiscible with the first and giving a distribution coefficient of favorable magnitude. The following table shows the results of an experimental test of the formula.

TABLE XII

9.86 cc. of 1.0305 normal HCl; 9.86 cc. of 1 normal Ethyl Acetate in Benzene. $C = 0.079$

t	$a-x$	k	k_2
2 hours.....	92.35	0.00326	0.000465
4 "	86.9	313	450
6.25 "	81.73	297	430
8 "	75.59	328	481
14.25 "	64.78	292	439
15.25 "	63.4	287	424
20.1 "	55.1	287	455
22.5 "	52.48	278	450

The third column gives the values of k calculated from the preceding equation. A slight drift in the values is discernible. Goldschmidt and Messerschmidt finally located the reason for this in the reversibility of the reaction. Ordinarily, in aqueous solution, the reverse process of esterification is negligible as compared with the hydrolytic process. With a benzene phase present, on the other hand, since the bulk of the ester is to be found in the benzene phase and relatively little in the aqueous phase, the reverse process becomes more important. Correction for this was introduced. The mathematical treatment is complex but the result is shown under k_2, a reasonable constant, free from drift, being obtained.

In a similar manner, Goldschmidt and Messerschmidt studied the alkaline hydrolysis of ethyl acetate with a benzene phase present, using aqueous baryta solution. The reaction in the aqueous layer is bimolecular with respect to the ester and the baryta. The modified reaction equation in such case is as follows:

$$k = \frac{1}{t}\cdot\frac{C+1}{C}\cdot\frac{x}{(a-x)a},$$[1]

[1] Cf. Treatment of Bimolecular Reactions, preceding chapter.

where a denotes respectively the ester and the baryta concentration. With different concentrations, respectively a and b, the equation becomes

$$K = \frac{1}{t}\frac{C+1}{C} \cdot \frac{1}{a-b} ln \frac{b(a-x)}{a(b-x)}.$$[1]

Goldschmidt and Messerschmidt neglected entirely the velocity in the benzene phase. This was undoubtedly justified owing to the slight solubility of water in benzene and to the distribution of hydrogen chloride between benzene and water which acid is certainly mostly in the aqueous layer. Such conditions may not always hold. Some experiments by Taylor and Close on the velocity of transformation of γ-hydroxy acids to lactones showed that the rate of conversion in wet ether solutions, 0.1 normal with respect to hydrogen chloride, was vastly more rapid than the rate of conversion in aqueous solutions of the same strength of catalyzing acid. It is apparent therefore that, in such a two-phase system, ether-water, the transformation of hydroxy acid to lactone would occur in both phases. The net rate would be composite of the rates in the two phases, and these would depend on the distribution of the hydroxy acid and catalyst between the two solvents and on the rates of reaction under the conditions set by such distribution.

Of reactions occurring in the main at the interface between two liquid phases the hydrolysis of a fat with the aid of "Twitchell's reagent" is a good example. Twitchell's reagent [2] is a sulphonic acid containing both an aromatic nucleus and a long hydrocarbon chain of the aliphatic type. Such acids act undoubtedly by virtue of their dual nature. The acidic grouping is soluble in water, the aliphatic hydrocarbon grouping in the oil. The aromatic stearo-sulphonic acid will therefore be concentrated at the interface between the oil and water, bringing these two reactants into mutual contact in a common complex, interaction being thereby facilitated. This may be looked upon as an increase of solubility of the fat in water acidified with the reagent. In such case, one would be dealing with a simple esterification in homogeneous medium. The mutual solubility may however be limited to simple molecular complexes and, as such, the reaction would be a reaction at an interface. The aromatic sulphonic acids, being strong acids comparable with hydrochloric acid, are therefore good catalytic agents for hydrolytic processes. They operate efficiently at temperatures in the neighborhood of 100° C., thereby enabling the splitting of the fat to be accomplished in open vessels with the use of live steam as the heating agent. A certain auxiliary efficiency of the Twitchell reagent is secured as a result of the emulsifying action of the reagent on oil-water mixtures, the emulsification increasing the effective area of interface. Lewkowitsch [3] cites the following data to illustrate the actual

[1] Cf. Treatment of Bimolecular Reactions, preceding Chapter.

[2] U. S. P. 628503 (1899); *J. Am. Chem. Soc.*, **22**, 22 (1900); *J. Am. Chem. Soc.*, **28**, 196 (1906): **29**, 566 (1907); *J. Ind. Eng. Chem.*, **9**, 194 (1917).

[3] Chemical Technology and Analysis of Oil, Fats and Waxes, Vol. I, sixth edition, p. 90. 1921.

fat-splitting efficiency of the naphthalene, anthracene and phenanthrene stearo-sulphonic acids in 1 per cent concentration on a neutral cotton seed oil heated in a current of steam.

TABLE XIII

REACTION RATE WITH TWITCHELL REAGENTS

Sulpho-stearo Aromatic Compound of	Hydrolysis after					
	$6\frac{1}{2}$ hrs.	13 hrs.	$19\frac{1}{2}$ hrs.	26 hrs.	$32\frac{1}{2}$ hrs.	39 hrs.
Naphthalene . . .	146.7	190.7	201.4	211.4	—	—
Anthracene.	2.5	21.8	76.3	170.7	186.5	190.7
Phenanthrene	45.7	125.7	177.7	183.6	194.1	201.2

The naphthalene compound shows itself in these experiments as the most efficient reagent.

REACTION VELOCITIES IN SOLID-GAS SYSTEMS

Vaporization of solids, condensation to the solid state, decomposition of solids to yield solid-gas systems, reactions between solids and gases and between gases at solid surfaces acting as catalytic agents are all examples of reactions which may be included in the general study of reaction velocity in heterogeneous solid-gas systems. The most striking advances in this field have been accumulated recently, mainly as a result of the investigations of Langmuir into the behavior of tungsten filaments heated in high vacua [1] and his more recent deductions [2] concerning the nature of the forces operative at an interface between the solid and the gaseous phase. The theoretical treatment which follows is largely drawn from the publications of Langmuir, frequently in his own words.

The Velocity of Vaporization: When a filament of platinum, or tungsten, or other metal is heated to a sufficiently high temperature in vacuum, the material evaporates. If the metal is placed in a uniformly heated enclosure, the evaporation from the surface will be gradually offset by the return of atoms of metal from the vapor which accumulates in the space. Finally, an equilibrium is reached in which the rate of condensation of the vapor is equal to the rate of vaporization.

Now the rate at which the saturated vapor comes into contact with the metal may be readily calculated from the principles of the kinetic theory when the vapor pressure is known. The calculation is similar to that of effusion of gases through small openings.[3]

[1] *J. Am. Chem. Soc.*, 1912-1916.

[2] *Phys. Rev.*, **2**, 331 (1913); **8**, 149 (1916). *J. Am. Chem. Soc.*, **38**, 2221 (1916). *Trans. Farad. Soc.*, **17**, 607, 621 (1921).

[3] Cf. Meyer's Kinetic Theory of Gases, German Edition, 1899, p. 82.

Consider a unit cube of the vapor one side of which is bounded by the metal. Half of the molecules in this unit volume are moving towards the metal and the other half are moving away from it. If ρ be the density of the gas, the mass of the gas moving towards the metal is $\frac{1}{2}\rho$.

Let Ω be the average (arithmetical) velocity of the molecules. It can readily be shown that the average component of the velocity in any given direction is $\frac{1}{2}\Omega$. Hence the average velocity with which the molecules in the mass, $\frac{1}{2}\rho$, are approaching the metal is $\frac{1}{2}\Omega$. The mass of gas, m, which strikes against the unit surface of metal per second is, therefore,

$$m = \tfrac{1}{4}\rho\Omega. \tag{1}$$

Assuming the gas laws,

$$\rho = \frac{pM}{RT}, \tag{2}$$

where p = pressure, M = molecular weight, T = absolute temperature and R = gas constant = 83.2×10^6 ergs per degree. The average velocity is given by the relation,

$$p = \frac{\pi}{8}\rho\Omega^2, \tag{3}$$

whence

$$\Omega = \sqrt{\frac{8RT}{\pi M}}. \tag{4}$$

Substituting (2) and (4) in (1), we get for the rate at which the vapor comes in contact with the metal

$$m = \sqrt{\frac{M}{2\pi RT}}\,p. \tag{5}$$

Expressing p in bars and placing $R = 83.2 \times 10^6$ egs per degree, this equation reduces to

$$m = 43.74 \times 10^{-6}\sqrt{\frac{M}{T}}\,p, \tag{6}$$

where m is expressed in grams.

If we can assume that every atom of the vapor which strikes the metal condenses, the equations (5) and (6) give the desired relation between the vapor pressure and the rate of evaporation in vacuo. If, however, a certain proportion, r, of the atoms of the vapor is reflected from the surface, then the vapor pressure will be greater than that calculated from the equations in the ratio $1 : (1 - r)$. As long ago as 1882, Hertz [1] pointed out theoretical considerations similar to those used above.

Experiments with many different metals have shown close agreement between the vapor pressures determined from the rate of evaporation in this way and the vapor pressures measured by processes which involve the forma-

[1] *Ann. Physik*, **17**, 177 (1882).

tion of saturated vapors. Knudsen [1] has made careful experiments of this kind with mercury vapor, while A. S. Egerton [2] has carried out determinations upon cadmium and zinc. Their results indicate that every atom of vapor condenses when it strikes the metal surface. An exceedingly careful investigation by Volmer and Estermann [3] confirms this result for liquid mercury surfaces. For solid mercury surfaces, the value of the accommodation coefficient,[4] $\alpha = 1 - r$, is somewhat less than unity (0.9–1.0) and dependent on temperature. For solid sulphur, phosphorus and benzophenone values of α between 0.2 and 0.5 were said to have been obtained by Volmer and Estermann, but no experimental details were given.

Knudsen [5] and Soddy and Berry [6] have shown from measurements of the heat conductivity of gases at low pressures that the number of molecules of a gas which are reflected from a smooth surface (i.e., do not reach thermal equilibrium with the surface) is as much as 70 per cent in the case of hydrogen but very much less with gases of higher molecular weight. The following table gives some of their results.

TABLE XIV

Gas	Surface	α
Hydrogen	Polished Platinum	0.36
Carbon Dioxide	Polished Platinum	0.87
Hydrogen	Platinized Platinum	0.71
Carbon Dioxide	Platinized Platinum	0.98

For gases of high molecular weight and for metal vapors in contact with a surface of the metal it is probable that the accommodation coefficient is in most cases unity.

Variation of the Rate of Evaporation with Temperature: The Clapeyron-Clausius formula gives the relation between vapor pressure and temperature:

$$\lambda = T\frac{dp}{dT}(V - Vo).$$

Neglecting the volume Vo of the solid in comparison with that of the vapor, V, and applying the gas laws, this equation becomes

$$\frac{dlnp}{dT} = \frac{\lambda}{RT^2}.$$

The heat of vaporization λ is a function of temperature such that

$$\frac{d\lambda}{dT} = C_g - C_s.$$

[1] *Ann. Physik*, **29**, 179 (1909).

[2] *Phil. Mag.*, **33**, 33 (1917).

[3] *Z. Physik*, **7**, 1 (1921).

[4] This term was suggested by Knudsen to indicate the fraction of the molecules which condense on striking.

[5] *Ann. Physik*, **34**, 593 (1911).

[6] *Proc. Roy. Soc.*, **84**, 576 (1911).

Here, C_v is the specific heat per mol. of vapor at constant pressure and C_s that of the solid per mol. For a monatomic metal vapor

$$C_v = 2.98 + R = 4.96 \text{ calories per gram atom.}$$

For tungsten,

$$C_s = 6.8.$$

Hence

$$\lambda = \lambda_0 - 1.8T.$$

Substituting this expression for λ in the Clapeyron-Clausius equation and converting to common logarithms, we obtain

$$\log p = A - \frac{0.218\lambda_0}{T} - 0.9 \log T, \tag{7}$$

where A is a constant of integration. Taking the logarithm of equation (5) in the preceding section, we obtain

$$\log m = \log p + \tfrac{1}{2} \log \frac{M}{2\pi R} - \tfrac{1}{2} \log T. \tag{8}$$

Combining equations (7) and (8), we therefore find

$$\log m = A' - \frac{0.218\lambda_0}{T} - 1.4 \log T, \tag{9}$$

where

$$A' = A + \tfrac{1}{2} \log \frac{M}{2\pi R}.$$

Equation (9) gives us the rate of evaporation of tungsten as a function of the temperature. Two empirical constants are to be determined from the experiments, namely, A' and λ_0. Experiments by Langmuir[1] at temperatures ranging from 2440° K. to 3136° K. showed that the rate of evaporation of tungsten in a vacuum over this temperature interval of 700° increased in the ratio 1 : 15,000. The vapor pressures were calculated and were found to agree excellently with the thermodynamical relations developed. The latent heat of vaporization of solid tungsten was found to be

$$\lambda = 217{,}800 - 1.8T \text{ calories.}$$

The rate of evaporation at any temperature in a perfect vacuum is given by the equation

$$\log m = 15.402 - \frac{47{,}440}{T} - 1.4 \log T,$$

[1] *Phys. Rev.*, 1, 329 (1913).

where m is the rate of evaporation in grams per square cm. per second. Similarly, the vapor pressure is given by the equation

$$\log p = 15.502 - \frac{47{,}440}{T} - 0.9 \log T.$$

Similar determinations on platinum and molybdenum were subsequently published by Langmuir and Mackay.[1] Other data on silver, gold, iron, copper and nickel are promised, those for silver being checked by another method due to von Wartenburg.

Rate of Sublimation in Air: The evaporation of small spheres of iodine in quiet air has been studied experimentally by H. W. Morse.[2] The experiments indicated that the particles remained spherical in shape throughout the experiment and that the rate of loss of weight was proportional (within an average error of one per cent) to the *radius* of the sphere and *not to its surface.* Langmuir has analyzed this remarkable result from the theoretical standpoint.[3]

In a study of the convection of heat from small wires in air and other gases Langmuir [4] found that the heat loss by "convection" consists essentially of conduction through a film of relatively stationary gas around the wire. According to the theory developed, the heat loss w is given by the equation

$$w = s(\varphi_1 - \varphi_2),$$

where s is the shape factor of the gas film, and $\varphi_1 - \varphi_2$ is equal to $\int_{T_1}^{T_2} k dT$,

where k is the heat conductivity of the gas and T_2 and T_1 are the temperatures of the wire and surrounding gas respectively. Good agreement between experiment and theory was found with a large number of gases at wire temperatures between 100° C. and the melting point of platinum. Applying the process of reasoning thus developed to the evaporation of small objects in air, Langmuir obtains an equation,

$$-\frac{dm}{dt} = s \int D d\rho. \tag{1}$$

Here $-dm/dt$ is the rate of loss of weight, s the shape factor, D the diffusion coefficient, ρ is the partial density of the vapor of the evaporating substance. For the low concentrations of vapor in question D will be assumed independent of ρ which may be expressed in terms of the gas laws by the equation

$$\rho = \frac{pM}{RT}. \tag{2}$$

[1] *Phys. Rev.*, **4**, 377 (1914).

[2] *Proc. Am. Acad. Arts Sci.*, **45**, April, 1910.

[3] *Phys. Rev.*, **12**, 368 (1918).

[4] *Phys. Rev.*, **34**, 401 (1912); *Proc. Am. Inst. Elec. Eng.*, **31**, 1011 (1912); *Trans. Am. Elec. Soc.*, **23**, 299 (1913).

For a spherical shell, the shape factor is [1]

$$s = \frac{4\pi ab}{b - a},$$

where b is the outside radius of the film of gas and a is the radius of the evaporating sphere. If a is small and negligible compared with b,

$$s = 4\pi a. \tag{3}$$

Substituting this together with (2) in (1), we get

$$-\frac{dm}{dt} = \frac{4\pi aDMp}{RT},$$

a result in direct agreement with the experimental observation that the rate of loss is proportional to the radius of the sphere. Calculating the diffusion coefficient from Morse's data, Langmuir found a value,

$$D = 0.053 \text{ cm. per sec.}$$

for iodine vapor in air at 20° C. No published data on the diffusion coefficient of iodine vapor in air appear to be available. The value is, however, a reasonable one when compared to other substances of high molecular weight. For carbon dioxide ($M = 44$) in air $D = 0.164$; acetic acid ($M = 60$), $D = 0.122$; butyric acid ($M = 86$), $D = 0.061$; benzene ($M = 78$), $D = 0.086$. The iodine molecule is heavier but of smaller cross section. The above value for $D = 0.053$ is also probably somewhat low, as the sphere was resting on a flat surface during the experiment, free diffusion in all directions being thereby hampered.

The results support the theory that the evaporation of small spheres is determined simply by the rate of diffusion through the surrounding air and that no allowance needs to be made for air currents. The results indicate also that the air in contact with the iodine surface is always saturated and that the actual rate of exchange of molecules between the solid iodine and its surrounding vapor is very rapid compared with the rate at which the vapor can diffuse away through the air. The theory can probably be applied to evaporation from all very small objects. In the case of larger objects experimental data must be obtained as to the thickness of the film through which diffusion occurs just as has been done in the case of convection. Rough experiments seem to indicate that the thicknesses of these relatively stationary films are practically the same for diffusion phenomena as for convection.

In amplification of this theory of Langmuir it may be observed also that as the rate of diffusion varies inversely with the pressure of the surrounding air in accordance with the equation

$$D_{760} = \frac{D_p \times p}{760},$$

[1] See *Trans. Am. Electrochem. Soc.*, **22**, 55 (1913).

the velocity of sublimation of small spheres should increase progressively with diminution of pressure. This is frequently observed experimentally in the case of substances subliming more or less readily at ordinary temperatures.

The Velocity of Condensation: In the discussion of the velocity of vaporization, an equation was developed which gives both the velocity of vaporization and condensation in its dependence on the vapor pressure, provided that the accommodation coefficient of the condensing molecules (or atoms) is unity

$$m = \alpha \sqrt{\frac{M}{2\pi RT}} p,$$

where α is now used to designate the accommodation coefficient. It was shown that, as this equation gave the correct values for vapor pressure in the case of a number of metals, the accommodation coefficient must in such cases be unity. The equation given above is therefore the general equation for velocity of condensation in its dependence on the pressure of the condensing vapor.

Knudsen and R. W. Wood independently arrived at the conclusion that mercury or cadmium atoms condense on a glass surface only if this surface is cooled below a certain critical temperature. Below this temperature, practically every atom is supposed to condense, while at temperatures materially above this critical point not one atom, out of thousands which strike the surface, condenses. This conclusion is not only inherently improbable in many ways, but is not capable of accounting for numerous experimental facts. Wood's and Knudsen's experiments are better explained by assuming that all the atoms of cadmium and mercury which strike a glass surface, even at high temperature, condense on the surface, but that at temperatures above the "critical temperature," the atoms re-evaporate before they have a chance to be struck by other atoms of the vapor. Langmuir has discussed this question in detail [1] and subsequently carried on experiments with cadmium vapor [2] which demonstrate conclusively that cadmium atoms evaporate rapidly from a clean glass surface at room temperature. There is no real reason for believing that cadmium may not also evaporate from glass at temperatures only slightly above the critical temperature of $-90°$ C. cited by Wood. Since molten cadmium does not wet glass, it is clear that the forces between a cadmium atom and a glass surface are much less than those between cadmium atoms, and the rate of evaporation should therefore be much higher than from a cadmium surface.

In most cases of adsorption we are dealing with a solid surface having a strong field of force, or a high potential energy per unit area, while on this solid is condensed a substance whose molecules possess a rather weak stray field of force. These are the conditions when ordinary gases condense on cooled surfaces of glass or metals. The forces which might tend to hold a

[1] *Phys. Rev.*, **8**, 149 (1916).
[2] *Proc. Nat. Acad. Sci.*, **3**, 141 (1917).

second layer of molecules are so weak that evaporation from the second layer occurs at a rate high compared with that from the first. Only with nearly saturated vapors, then, can a second layer form.

With cadmium and mercury vapors condensing on glass, however, we have a case in which the evaporation from the second layer takes place much more slowly than from the first layer. We see, therefore, that a kind of instability necessarily results. There is considerable difficulty in getting the first layer to form, because the atoms tend to evaporate before the others are able to condense on top of them or beside them. If the first layer ever does form, then the evaporation practically ceases and successive layers are then formed with ease. This view seems to give a clear picture of the mechanism of the formation of nuclei on which condensation occurs. The formation of frost crystals on a greasy window pane, or Moser's breath figures on glass, are illustrations of effects of this kind.

Volmer and his coworkers [1] have amplified this method of treatment of condensation processes and have made interesting studies of the method of crystal growth from vapors by condensation. Volmer employs Langmuir's equation in the form

$$m = \alpha \frac{1}{\sqrt{2\pi R}} \sqrt{\frac{M}{T}} (p_D - p_K),$$

where p_D is the saturated vapor pressure, p_K that of the condensate in contact with the vapor, the other symbols having their previous significance. Now, since

$$v = \frac{m}{s},$$

where s is the specific gravity of the condensed substance and v is the rate of growth normal to a surface of unit area on which m grams per second are deposited, the equation may be written

$$v = \frac{1}{s} \alpha \frac{1}{\sqrt{2\pi R}} \sqrt{\frac{M}{T}} (p_D - p_K),$$

or, where p_K is negligible compared with p_D,

$$v = \frac{1}{s} \alpha \frac{1}{\sqrt{2\pi R}} \sqrt{\frac{M}{T}} p_D.$$

Volmer and Estermann have employed this equation in an analysis of the growth of mercury crystals on a glass surface cooled to − 63° C., the vapor being supplied from liquid mercury in a high vacuum and at a temperature of − 10° C. Under these conditions no separation of mercury is observed in the first minute after cooling the condensing surface to − 63° C. After a

[1] *Z. Physik*, **5**, 31, 188 (1921). *Z. Physik*, **7**, 1, 13 (1921). *Z. physik. Chem.*, **102**, 267 (1922).

minute, however, single small crystal flakes become visible, which microscopic observation shows to be extraordinarily thin hexagonal leaflets the thickness of which is, at a maximum, 1×10^{-4} of the diameter of the hexagonal face. An interesting feature of the growth in the earlier stages is that the flakes are seen to vibrate in irregular movements, which are quite independent of any external vibrations and appear to be due to molecular collisions between vapor molecules and the leaflets, analogous to the Brownian movement. The leaflets attain a breadth of about 0.3 mm. before they seem to increase noticeably in thickness.

The extraordinary growth in two directions while the thickness of the plates remains so small, might seem at first to indicate an extremely low value for α, the accommodation coefficient, along one face. That this cannot be true, however, is evident when it is remembered that direct experiment has shown that α for all faces of solid mercury in this temperature interval is between 0.9 and unity, so that but few molecules can be reflected from all faces.

The explanation of the discrepancy comes as a result of the quantitative application of the above equation. Employing p_D for mercury at $-10°$ C., it can be calculated that the maximum value for v is 2.5×10^{-7} cm. per second. Hence, in one minute, the maximum growth in any dimension with mercury at $-10°$ C. should be $2 \times 60 \times 2.5 \times 10^{-7}$ cm. $= 3 \times 10^{-5}$ cm. per minute, since growth may occur on two opposite faces. Actually, the leaflets attain an observed breadth of 3×10^{-2} cm. per minute or in other words, 1000 times greater than the calculated growth. This observation definitely disproves the assumption that the crystal growth is *merely* a question either of condensation or reflexion of impacting molecules. Volmer is led therefore to the conclusion that along the face of the leaflets, the molecules condensing are held temporarily in the force field of the surface, retaining, however, their motion until they either (1) evaporate or (2) are attracted to and held at the edges of the surface or (3) through contact with other molecules form the nucleus of another lattice layer. The probability of (1), (2) or (3) occurring must depend upon the vapor density and on the size of the surface. The probability of (1) is in any case very small, for reasons already cited. The probability of (2) will be greater the smaller the breadth of the crystal plate. As this breadth increases, (3) will be more important, which appears to be true when the leaflets have attained a length and breadth of 0.3 mm., for then the plates begin more rapidly to increase in thickness. Quantitative studies of the rates of crystal growth are promised. What has been accumulated already, however, demonstrates clearly that crystals are obtained from directed streams of vapor molecules and that the growth of crystal faces from vapors is a somewhat complex process.

Velocity of Chemical Reactions between Gases and Solids: Langmuir's studies of the behavior of gases at low pressures in contact with tungsten at high temperatures in filament lamps are instructive as to the mechanism of such reactions. At low gas pressures, the equation previously developed

(equation (6) page 971) may be used in a slightly modified form to express the number of gram molecules, μ, of any gas of molecular weight M striking unit surface per second,

$$\mu = 43.74 \times 10^{-6} \frac{p}{\sqrt{MT}},$$

s nce

$$\mu = \frac{m}{M}.$$

If the accommodation coefficient be again α, the rate at which the gas condenses on the surface will be

$$\alpha\mu = 43.74 \times 10^{-6} \frac{\alpha p}{\sqrt{MT}}.$$

That the effective surface for such condensation was not the total surface area of the filament was obvious however from Langmuir's experiments on the electron emission from heated tungsten filaments in the best available vacua. Oxygen or water vapor, even at temperatures as high as 1900° K., decreased the emission many thousandfold by pressures of oxygen as low as one bar (one dyne per sq. cm., or approximately 1×10^{-6} atmospheres). This undoubtedly indicates that the larger part of the surface is covered with an extraordinarily stable film of combined oxygen which persists at these high filament temperatures even in a high vacuum. The film is not a film of tungstic oxide, WO_3, since, above 1200° K. in a vacuum, this oxide distils off as fast as it is formed.

When the filament is heated to 3300° K. and a pressure of oxygen of a few bars is admitted to the bulb, the rate of disappearance of the oxygen shows that about 50 per cent of all the oxygen molecules which strike the filament, as calculated by the equation previously cited, react with the filament to form WO_3 which distils on to the bulb. Since there are three atoms of oxygen in the molecule of this compound and only two in the oxygen molecule, it is clear that at least one half of the tungsten surface, even at this high temperature, must be covered with oxygen in some form. The remarkable stability of these oxide films, as well as the complete change in the chemical properties of the oxygen (the oxygen film on the tungsten surface is quite inactive towards hydrogen even at 1500° K.), gives reason for believing that the surface is covered with individual oxygen atoms chemically combined with the underlying tungsten atoms. The film cannot be regarded as consisting of an oxide of tungsten, nor as atomic oxygen, in the sense in which we think of free oxygen atoms. The oxygen atoms are probably held to the surface by four pairs of electrons, just as the oxygen atom is held to the carbon atom in CO_2. The oxygen atoms are thus chemically saturated, but the tungsten atoms are not saturated, so that they are held by strong forces to the tungsten atoms that lie below them. This kind of structure is quite in accord with the conception

of the structure of solids to which we are led by the work of the Braggs on crystal structure.

Work with other metals has shown that stable films of the kind we have just been discussing are of very common occurrence. Oxygen forms a similar film on carbon, and carbon monoxide, hydrogen cyanide, hydrogen sulphide, phosphine, and arsine form stable films on platinum. It is probable that all substances that have a poisoning effect on catalytic surfaces form films of this kind, of greater or less degree of stability.

This concept of the behavior of a tungsten filament surface towards oxygen at low pressures was shown by Langmuir to be in complete agreement with his results on the reaction of oxygen with such heated filaments. The velocity of reaction was shown to be proportional to the pressure of oxygen, in agreement with the equation for the rate at which the oxygen reaches the surface. Furthermore, by dividing the rate at which "clean-up" of oxygen occurred by the rate at which the oxygen reached the surface at a given pressure, it was possible to determine what fraction, E, of all the molecules striking the surface reacted with the surface. The following table shows the value of E, calculated from the reaction measurements at different temperatures and found to be independent of the pressure at a given temperature.

TABLE XV

	Temperature K.								
	1070°	1270°	1470°	1570°	1770°	2020°	2290°	2520°	2770°
E.....	0.00033	0.0011	0.0053	0.0094	0.0255	0.049	0.095	0.12	0.15

Experiments were made with the bulb cooled by liquid air and also heated to 300° C. in an oven. The rate of reaction was found to be independent of the bulb temperature.

The reaction between carbon filaments and oxygen at low pressures was similarly studied. Again, evidence for the formation of stable oxygen films on the surface of the carbon was obtained, the film being produced either from oxygen or carbon dioxide. At high temperatures, e.g., 2200° K., in good vacua, the oxygen thus combined leaves the filament as carbon monoxide. In the lower temperature regions, 1200–1700° K., the oxygen clean-up was accompanied by the formation of some carbon dioxide and some oxide film, the production of which materially slows up the disappearance of oxygen.

Study of the kinetics of reaction between tungsten and nitrogen, tungsten and carbon monoxide, molybdenum and nitrogen, platinum and oxygen showed definitely that the reaction in these cases was between metal vapor and gas. The gas disappears at a given temperature at a rate which is independent of the gas pressure. With nitrogen, a compound WN_2 was formed. The reaction velocity increased with temperature at a rate equal to that of

the increase in the rate of vaporization with temperature. By operating at low pressures, it was established that the coefficient E was unity, or, in other words, practically every collision between a tungsten atom and a nitrogen molecule resulted in the formation of the compound. With carbon monoxide a peculiarity was observed. With the bulb at room temperature the gas behaved like nitrogen. With the bulb in liquid air, however, the rate of clean-up was five times as fast as with the bulb at room temperatures. This set of observations is distinctly worthy of further investigation.

Reactions at Solid-Solid Interfaces: Faraday observed that a perfect crystal of sodium carbonate decahydrate or sodium sulphate decahydrate refuses to effloresce until the surface is scratched or broken and that the efflorescence then spreads from the injured place. Similar phenomena have been observed with other crystals. It is especially noteworthy in the case of cadmium sulphate crystals, which are readily obtained in large, perfect form. The crystals, in this condition, lose no weight for weeks on standing in a moisture-free space. In such cases it is necessary to assume that the reaction (dehydration) occurs only at the boundary between two phases. Langmuir [1] has analyzed the general problem of the kinetics of a reaction occurring with separate phases of constant composition, for example, the dissociation of calcium carbonate. From kinetic considerations one would expect that the rate of decomposition of a surface layer of calcium carbonate would be proportional to the fraction θ_2 of the surface occupied by the calcium carbonate. Similarly, the formation of calcium carbonate would be determined by the carbon dioxide pressure and by the fraction θ_1 of the surface covered by calcium oxide. At equilibrium, equating these two rates, we should obtain

$$p\theta_1 = K\theta_2, \tag{1}$$

where K is the equilibrium constant. These assumptions therefore would make p dependent on the ratio, θ_1/θ_2, which is contrary to experimental fact. The above result, however, is what would be expected in the light of the Phase Rule if there were a single solid phase of variable composition, instead of two solid phases of constant composition. It would apply to the dissociation of ferrous-ferric oxide studied by Sosman and Hostetter [2] who found "a continuous series of solid solutions from Fe_2O_3 to a point very near Fe_3O_4." The assumptions made in the above derivation are obviously not consistent with a dissociation involving two distinct solid phases. In order that calcium carbonate may dissociate and form a phase of calcium oxide (instead of a solid solution) it is necessary that *the reaction shall occur only at the boundary between two phases.* Thiel,[3] treating the same subject, accepts Equation (1) and hence concludes that θ_1/θ_2 is necessarily constant at a given temperature even for two solid phase systems. Experimental evidence, however, is at variance with this assumption. The dissociation pressure of a pair of salt hydrates

[1] *J. Am. Chem. Soc.*, **38**, 2263 (1916).

[2] *J. Am. Chem. Soc.*, **38**, 807 (1916).

[3] *Sitz. Ges. Bef. gesamt. Naturwiss.*, Marburg, 1913.

is not a function of the relative amounts of both present. Langmuir is therefore led to the conclusion that the building up or breaking down of a solid phase in such systems occurs only at the interface between the two phases. He shows that this viewpoint is in good agreement with what is now known as to the orientation of the atom groupings in the crystal lattice..

Enhanced activity of this type at solid-solid interfaces is really quite common as a study of the literature and experimental work by Taylor and his coworkers [1] has revealed. Thus, in a determination of the dissociation pressure of sodium bicarbonate, Lescoeur [2] observed that "the development of pressure occurs slowly at first, then more quickly toward the end. . . . It has seemed to me that the final equilibrium was obtained more rapidly the more the proportion of dissociated salt increased." The dissociation of silver oxide, studied by G. N. Lewis [3] is a parallel case, it being observed that the rate of dissociation increased with increasing production of silver. The different nature of the dissociation process when such interfaces are not set up is well illustrated in the case of mercuric oxide studied by Hulett and G. B. Taylor.[4] In this case, at temperatures where dissociation becomes marked (500° C.), the mercury formed is also vaporized. No interface results and no acceleration of the dissociation is observed. As a result, passage of nitrogen gas for twenty-four hours over pure mercuric oxide at 500° C. gave concentrations of oxygen corresponding to only a few mm. pressure, whereas the true equilibrium pressure at that temperature was upwards of one atmosphere. When interfaces were produced by the addition of foreign substances, iron oxide, manganese dioxide and platinum, true equilibrium pressures were at once established. Recent researches of Kendall and Fuchs [5] on the accelerated decomposition of silver oxide, mercuric oxide and barium peroxide in presence of other oxides is also illustrative of the effect produced by the deliberate creation of interfaces. The investigations of Hinshelwood and Bowen [6] on the rate of oxygen evolution from various salts, of Hinshelwood [7] on the stability of trinitrophenylmethylnitroamine, of Sieverts and Theberath [8] on the kinetics of the decomposition of silver permanganate, in all of which a reaction velocity autocatalytic in nature is obtained, are further evidence of this phenomenon of interface activity. The reaction is negligibly small at the outset, but as the area of interface grows, the velocity increases accordingly. In the work by Fry and Otto [9] on the rate of decomposition of potassium perchlorate, the reaction is interpreted by them as a unimolecular reaction but is in reality an autoaccelerated reaction of the interface type.

[1] Taylor, *J. Franklin Inst.*, **197**, 1 (1922).
[2] *Ann. Chim. Phys.*, (6) **25**, 430 (1892).
[3] *Z. physik. Chem.*, **52**, 310 (1905).
[4] *J. Phys. Chem.*, **17**, 567 (1913).
[5] *J. Am. Chem. Soc.*, **43**, 2017 (1921).
[6] *Phil. Mag.*, (6) **40**, 569 (1921).
[7] *J. Chem. Soc.*, **119**, 721 (1921).
[8] *Z. physik. Chem.*, **100**, 463 (1922).
[9] *J. Am. Chem. Soc.*, **45**, 1138 (1923).

The rate of reaction between a solid and a gas may also be determined by the establishment of interfaces between the initial solid phase and that produced by the reaction. This is well illustrated in the study of Pease and Taylor [1] on the rate of reduction of copper oxide by hydrogen, and of Jones and Taylor [2] on the reduction by carbon monoxide. It has been shown that low temperature reduction by these gases is negligible until copper nuclei are established in the reaction mass. Subsequent reaction is then confined to the boundaries between the copper and copper oxide as can be demonstrated visually by the ever-increasing area of the red copper extending outwards from the original nuclei. The amounts of water vapor and carbon dioxide produced per unit of time as a result of such reduction increase steadily with increasing extent of interface; they attain a maximum and then steadily diminish as the reduction of the oxide is completed. Nickel oxide, NiO, and vanadium pentoxide show the same phenomenon. In the latter case, the interface is visible owing to the change from a red-brown to a blue-black oxide. Oxides which form, with a lower oxide, a continuous series of solid solutions should not, on the basis of this theory, show an accelerating rate of reduction at a given temperature.

Gas Reactions at a Solid Catalyst Surface: The pioneer investigations in this branch of the subject of reaction kinetics are due to Bodenstein and his coworkers in the early years of the present century. Reactions of this type form the most important of the technical catalytic reactions and include the contact sulphuric acid process, the synthesis of ammonia from the elements, the oxidation of ammonia to nitric oxide, the Deacon chlorine process, surface combustion processes and numerous contact oxidation, hydrogenation and dehydrogenation processes in the vapor phase. The problem of mechanism in such reactions is therefore of first importance and the approach to this problem via a study of reaction kinetics is undoubtedly the surest.

The researches of Bodenstein and his coworkers established quite definitely that such reactions at solid surfaces are not of the reaction order which would be deduced from the stoichiometric equation. Thus Bodenstein and Fink [3] showed that the reaction,

$$2SO_2 + O_2 = 2SO_3,$$

occurring at a platinum surface, was not a trimolecular reaction. On the contrary, the reaction was, in the majority of experiments, proportional to the sulphur dioxide concentration, independent of the oxygen concentration, and inversely proportional to the square root of the sulphur trioxide concentration under various conditions of gas concentration. The reaction equation became, therefore,

$$+\frac{d(SO_3)}{dt} = k\frac{(SO_2)}{(SO_3)^{1/2}}.$$

[1] *J. Am. Chem. Soc.*, **43**, 2179 (1921).
[2] *J. Phys. Chem.*, **27**, 623 (1923).
[3] *Z. physik. Chem.*, **60**, 1 (1907).

Bodenstein and Ohlmer [1] similarly found that the reaction between oxygen and carbon monoxide in contact with quartz glass takes place at a rate proportional to the pressure of the oxygen and inversely proportional to the pressure of carbon monoxide. In contact with crystalline quartz, however, the reaction followed the ordinary stoichiometric equation. Bodenstein and Kranendieck [2] found that the rate of decomposition of ammonia by heated quartz glass is proportional to the square root of the pressure.

In seeking an explanation of such experimental facts, Bodenstein and Fink were led to propound a modified form of the Nernst theory of heterogeneous reactions. They assumed that what in reality was being measured was the rate of diffusion of the reacting gases through a film of gas adsorbed on the surface of the catalyst. They considered that the film varied in thickness with variation in the partial pressure of the gas in contact with the solid. Thus, in the case of sulphur trioxide formation, the reaction was supposed to occur by diffusion of sulphur dioxide through a film of adsorbed sulphur trioxide the thickness of which was proportional to the square root of the partial pressure of the sulphur trioxide present in the gas phase. The oxygen, which was without influence on the reaction, was assumed to diffuse rapidly through this layer as compared with the sulphur dioxide. Similarly, in the case investigated by Bodenstein and Ohlmer, the oxygen was assumed to diffuse through an adsorbed layer of carbon monoxide the thickness of which layer was proportional to the square root of the partial pressure of carbon monoxide. In verification of this theory, Fink measured the amount of sulphur trioxide adsorbed by the platinum per unit area. It is significant, in view of later work, that he found it to be of the order of magnitude of a single layer of molecules. This last fact, if adequately realized at the time, might have suggested the inherent difficulty of assuming that the thickness of the film could vary in proportion to the square root of pressure over wide variations of pressure.

That adsorption of reacting gases on the catalyst surface was of primary importance in determining the reaction rate at such surfaces was very decisively demonstrated by the interpretation by Stock and Bodenstein [3] of the results of Stock, Gomolka and Heynemann [4] on the rate of decomposition of arsine, AsH_3, on arsenic surfaces. The reaction velocity was representable by an equation of the form,

$$-\frac{dc}{dt} = kc^{0.5},$$

the exponent of c, the gas concentration, indicating a distribution between gas space and surface following the ordinary Freundlich adsorption isotherm.

The data presented previously on the phenomena of evaporation from and condensation on solid surfaces as interpreted by Langmuir leads to a very

[1] *Z. physik. Chem.*, **53**, 175 (1905).
[2] Nernst Festschrift, p. 99.
[3] *Ber.*, **40**, 570 (1907).
[4] *Ber.*, **40**, 532 (1907).

definite interpretation of the phenomenon of adsorption. From Langmuir's viewpoint, adsorption is the result of the time lag between condensation and evaporation. The rate of evaporation is determined by the nature of the forces operative at the surface between solid and gas. These forces are essentially chemical in nature and determined by the unsaturation of the surface atoms in the solid body. Furthermore, these forces are limited in range to distances of the order of molecular thickness. The present conception of atoms consisting of electrons arranged in space about a positively charged nucleus, giving as a whole an electrically neutral unit, leads inevitably to the conclusion that the field of force surrounding the neutral atom or molecule must decrease in intensity with a very high power of the distance from the center. Born and Landé have calculated that the electric force around a group of eight electrons arranged at the corners of a cube and surrounding a nucleus having an equivalent positive charge is inversely proportional to the tenth power of the distance between them. Debye, from another viewpoint, deduces that the force of attraction between molecules is inversely proportional to the eighth power of the distance between them. Such data lead directly to the conclusion that appreciable forces cannot be transmitted in space through distances much greater than molecular diameters. A surface covered with a layer of gas molecules should show, therefore, little tendency to accumulate a second layer of such a gas. In Langmuir's view, a surface covered with oxygen molecules should show little more tendency to form a second layer than there would be for these molecules to remain in the surface of liquid oxygen at the same temperature. Only with saturated vapors should films of gas molecules ever be obtained. The evidence obtained by a study of oil films on water strengthens the argument for the unimolecular film theory and suggests also that in all cases of adsorption the possibility of orientation of molecules must be considered.

The surface of a catalyst is, on this view, to be regarded as an area containing a definite number of elementary spaces, in which some of the spaces are vacant while others are covered by atoms or molecules. The activity of the surface is conditioned by the nature of, the arrangement and spacing of the atoms in the surface layer, and relatively independent of the atoms below the surface. The velocity of reaction on such surfaces depends on the fraction of such surface which is covered by adsorbed substances, and this in turn depends on the velocity with which the molecules strike the surface and on the rate of evaporation of the molecules therefrom. This concept can be developed to yield a quantitative formulation of the kinetics of such catalytic gas reactions at solid surfaces. Langmuir has developed two cases of such in detail.

First Case: Surface only covered to small extent: Consider a single gas undergoing a chemical change in contact with a solid body. Let θ be the fraction of the surface unoccupied and θ_1 be the fraction occupied by adsorbed atoms or molecules. If each molecule condensing requires only one elementary space, the rate of condensation will be

$$\alpha\theta\mu,$$

where the several symbols have the significance already ascribed to them in earlier equations. If a molecule requires two spaces for condensation, the rate will be

$$\alpha\theta^2\mu,$$

for, the chance that one space is vacant is θ, but the chance that two given spaces will be simultaneously vacant is θ^2. In general, therefore, the rate of condensation will be

$$\alpha\theta^n\mu,$$

where n is an integer indicating the number of spaces in the surface occupied by one adsorbed molecule. Similarly the rate of evaporation will in general be proportional to θ_1^n or equal to $k_1\theta_1^n$, where k_1 is the proportionality factor.

With a surface covered to only a slight extent, θ is essentially equal to unity and so, at equilibrium, when vaporization is equal in rate to condensation,

$$\alpha_1\mu_1 = k_1\theta_1^n.$$

Now, the product of the chemical reaction is formed from the adsorbed film by the combination of the substance from m adjacent spaces. In the case of a dissociation m will be unity. If v represents the velocity of the chemical change,

$$v = k_2\theta_1^m.$$

Combining these two equations,

$$v = k_2\left(\frac{\alpha_1\mu_1}{k_1}\right)^{m/n}.$$

The velocity of the reaction thus varies with the m/nth power of the pressure of the gas since μ is directly proportional to the pressure.

The equation corresponds directly to many cases already studied. In the dissociation of hydrogen molecules by a heated wire, $m = 1$ and $n = 2$. The velocity of dissociation should therefore be proportional to the square root of the pressure of molecular hydrogen. The recombination of hydrogen atoms in contact with a heated wire, however, takes place in proportion to the square of the pressure of the atomic hydrogen. Langmuir verified these conclusions experimentally. The results of Bodenstein and Kranendieck on ammonia and of Stock and Bodenstein on arsine previously detailed are similarly interpretable, assuming that one ammonia or one arsine molecule occupies two elementary spaces. Bodenstein and Ohlmer's observation that the reaction between carbon monoxide and oxygen in contact with crystalline quartz is inversely proportional to the square root of the oxygen concentration and directly to the carbon monoxide concentration is also in accord with the theory. For, if we assume carbon monoxide occupies one elementary space and an oxygen molecule two spaces (i.e., present on the surface as atoms), we obtain

$$\begin{aligned}\alpha_1\mu_1 &= k_1\theta_1,\\ \alpha_2\mu_2 &= k_2\theta_2^2,\\ v &= k_3\theta_1\theta_2,\end{aligned}$$

where the subscript 1 refers to carbon monoxide, 2 refers to oxygen, 3 refers to carbon dioxide. These equations give

$$v = \frac{k\mu_1}{\sqrt{\mu_2}},$$

where k is a constant involving α_1, α_2, v_1, etc.

Second Case: Surface nearly completely covered: Consider a reaction in which two gases are in contact with a solid body. One of the gases (subscript 1) is present in such quantity and evaporates so slowly that the surface remains nearly completely covered by an adsorbed film of this substance. A second gas (subscript 2) undergoes a chemical change when its molecules come in contact with the uncovered surface. The rate at which the first gas will condense is $\alpha_1\theta^n\mu_1$, where n is the number of elementary spaces occupied by each molecule which condenses. Therefore, for equilibrium,

$$\alpha_1\theta^n\mu_1 = k_1,$$

since θ_1 will be small and constant. The rate at which the second gas will enter into the reaction will be proportional to $\mu_2\theta^m$. In general, the exponent m will be unity. It may however be integral or even fractional. Assuming $m = 1$, we get for the velocity of reaction

$$v = k_2\theta\mu_2.$$

Combining these equations, we find

$$v = k_2\mu_2\left(\frac{k_1}{\alpha_1\mu_1}\right)^{1/n}.$$

The velocity of reaction is thus proportional to the pressure of the gas 2 and inversely proportional to the nth root of the gas 1.

It will be observed that this solution is that obtained by Bodenstein and Fink for the oxidation of sulphur dioxide at platinum surfaces, in which case $n = 2$ for sulphur trioxide. It holds true for Bodenstein and Ohlmer's work on carbon monoxide oxidation in contact with quartz glass in which the rate was inversely proportional to the pressure of carbon monoxide. Hence for carbon monoxide on quartz $n = 1$.

Langmuir [1] has given a very comprehensive and detailed analysis of the theory embracing many more cases than those discussed above. He has applied this analysis to his own experimental work on the mechanism of oxidation of carbon monoxide and hydrogen at platinum surfaces. The following paragraphs summarize his conclusions.

Carbon Monoxide and Oxygen: When mixtures of carbon monoxide and oxygen at pressures up to a few hundred bars (0.1 mm.) are brought into contact with a smooth platinum surface at 500° to 700° K., they react at a rate proportional to the partial pressure of oxygen and inversely proportional to

[1] *Trans. Farad. Soc.*, 17, 621 (1921).

the pressure of monoxide. The reaction velocity increases rapidly with the temperature, about 1.6 fold for 10° at 600°.

With the platinum at 750° to 1050° K., the velocity is practically independent of the temperature, being limited largely by the rate at which the gases can come into contact with the surface. With an excess of oxygen, the velocity is proportional to the pressure of monoxide, while, with an excess of monoxide, the rate is proportional to the pressure of the oxygen.

A theoretical quantitative analysis of the experimental results leads to the following conception of the mechanism of the reaction. Every oxygen molecule which strikes a *clean* platinum surface condenses on the surface in the form of single atoms combined with separate platinum atoms. This chemical union is so firm that there is no appreciable evaporation of the oxygen atoms from the surface even with the platinum at 1500° K. These adsorbed oxygen atoms are in a very active condition in regard to their ability to react with monoxide; for, *every* molecule of carbon monoxide which strikes an adsorbed oxygen atom reacts with it to form dioxide. When monoxide molecules strike a clean platinum surface, every one condenses on the surface, being held by chemical union between the carbon atom and two platinum atoms. An adsorbed film of monoxide thus consists of a unimolecular layer of oriented molecules. These adsorbed molecules are not as firmly held to the surface as oxygen atoms, for they evaporate at an appreciable rate at temperatures as low as 500° K. Because of their orientation the monoxide molecules are very inert chemically towards oxygen. At 500° K. only about one oxygen molecule out of 10^{12} which strike a surface covered with adsorbed monoxide reacts with the monoxide. The heat of evaporation of adsorbed monoxide is 31,800 calories per gram molecule; and, at 700° K., with a pressure of one bar of monoxide, at least half of the platinum surface is covered with adsorbed monoxide.

In the low temperature range, the surface is nearly completely covered by a monoxide film, and the reaction occurs only when monoxide molecules strike oxygen atoms which have become adsorbed in the spaces left vacant by the evaporation of monoxide molecules.

In the high temperature range, the surface is nearly covered with oxygen when there is an excess of oxygen, and the reaction velocity is then limited by the rate at which the monoxide strikes the surface. With an excess of monoxide the surface is largely bare. The reaction velocity is limited by the rate at which the oxygen strikes the surface, for every oxygen molecule remains on the surface (in atomic condition) until struck by a monoxide molecule.

Hydrogen and Oxygen: At low temperatures (300° to 600° K.) rather erratic results are obtained for the reaction velocity with mixtures of hydrogen and oxygen, for the velocity depends upon the previous treatment of the platinum. When the platinum is in a relatively inactive condition, the results are similar to those obtained with carbon monoxide and oxygen, the velocity being roughly proportional to the pressure of oxygen and inversely to that of the hydrogen.

At high temperatures (700° to 1900° K.) the results correspond closely to those obtained with monoxide, the hydrogen having the same function as the

monoxide. At these temperatures, the reaction is not sensitive to the previous treatment of the platinum.

These results indicate that the adsorbed oxygen atoms are very reactive towards hydrogen, every collision between a hydrogen molecule and an adsorbed oxygen atom resulting in combination. Under certain conditions adsorbed hydrogen atoms are relatively inactive towards oxygen molecules, but the platinum can be brought into a condition which enables the adsorbed hydrogen to react with oxygen molecules or with the oxygen adsorbed in adjacent spaces on the surface.

That the mechanism of oxidation of these two gases is quite specific and may be different in the case of each is very evident from the studies of Pease and Taylor [1] and Jones and Taylor [2] on the mechanism of these oxidations in the presence of copper oxide, copper and nickel. With hydrogen and copper oxide, the mechanism is undoubtedly alternate reduction and oxidation. In presence of reduced copper, catalysis of hydrogen-oxygen mixtures is also determined by alternate oxidation and reduction. With reduced nickel, this is certainly not the case. Reaction at nickel surfaces is apparently the oxidation of hydrogen adsorbed on the nickel, the reaction occurring freely, in presence of an active catalyst at room temperatures. With carbon monoxide and oxygen in presence of reduced copper, the reaction is similar to that with hydrogen and oxygen on nickel, in marked contrast to that obtaining with these latter gases on copper. The mechanism is not an alternate oxidation and reduction but an oxidation of adsorbed carbon monoxide, in agreement with the high adsorptive capacity of copper for carbon monoxide and its low capacity for hydrogen and oxygen as revealed by the adsorption measurements of Taylor and Burns.[3]

The intimate connection between adsorptive capacity and catalytic activity in gas reactions at solid surfaces is further revealed in the studies of Pease [4] on the reaction velocity of the ethylene-hydrogen combination in presence of copper. In this study, both the kinetics of the reaction and the adsorption of the several gases singly and in mixtures were measured on the same catalyst. The study showed that the rate of reaction at 0° C. was determined mainly by the rate at which the hydrogen reached the catalyst surface, which surface was, however, largely covered with ethylene. At 200° C. the reaction approximated to a bimolecular reaction. This work of Pease constitutes perhaps the most thorough investigation in which catalytic activity and adsorption have been studied in parallel. There is evidence in this work as well as in other investigations conducted in Princeton that on a catalyst surface there are positions of varying adsorptive capacity and catalytic activity. It is possible to destroy the adsorptive capacity of a sample of copper for hydrogen without considerably reducing the adsorptive capacity for ethylene. So treated, however, the surface becomes inactive for the hydrogenation process.

[1] *J. Am. Chem. Soc.*, **43**, 2179 (1922).
[2] *J. Phys. Chem.*, **27**, 623 (1923).
[3] *J. Am. Chem. Soc.*, **43**, 1273 (1921).
[4] *J. Am. Chem. Soc.*, **45**, 1196, 2235, 2296 (1923).

Benton's researches [1] on the adsorptive capacity of oxides for carbon monoxide, hydrogen and other gases illustrate also the effect of adsorption in determining the relative rates of two reactions. As is well known,[2] in presence of certain oxides, carbon monoxide can be oxidized preferentially by gaseous oxygen in presence of hydrogen even though the latter be present to the extent of 99 per cent of the gas mixture. Benton's measurements reveal that carbon monoxide is adsorbed to a very much greater extent than hydrogen so that, at the surface of the catalyst, it probably predominates almost exclusively.

These kinetic and adsorption studies do not answer, however, the problem presented by the well-known specificity of solid catalysts. This is well illustrated in the measurements of Taylor and Burns [3] and of Gauger and Taylor.[4] Nickel, cobalt, iron, palladium, platinum and copper all show marked adsorption of carbon monoxide and hydrogen. The two latter, however, are quite inactive in the catalysis of the reactions

$$CO + 3H_2 = CH_4 + H_2O,$$
$$2CO = CO_2 + C,$$

whereas the three catalysts first named are quite active. Both copper and nickel adsorb both benzene and hydrogen. Nickel alone is markedly active in hydrogenation of the aromatic nucleus.[5]

Langmuir has emphasized in this regard that with more or less complicated organic molecules the orientation of the molecules and steric hindrance effects become more important as factors in the mechanism of the reaction. Furthermore, actual distances between the surface atoms of the catalyst are undoubtedly of importance. The changes which a smooth stranded gauze of platinum undergoes when used as catalyst for ammonia oxidation, which changes are accompanied by enhanced activity, are probably changes, in Langmuir's view, involving differences in geometrical arrangements of the surface atoms favoring higher activity. Similar changes occur in platinum employed for hydrogen-oxygen catalysis. The increased activation thus resulting does not, however, change the velocity observed in the reaction between carbon monoxide and oxygen. Hence, activation for one reaction is not necessarily activation for another reaction.

In certain cases, however, it is not possible to account for specificity of contact agent on the basis of oriented adsorption alone. The varying activity of reduced metals in decomposing ammonia into the elements is a case in point. A large variety of metals show adsorptive capacity for ammonia, as, for example, iron, molybdenum, tungsten, nickel, copper, sodium; the nature of the

[1] *J. Am. Chem. Soc.*, **45**, 887, 900 (1923).

[2] Harger and Terry, Brit. Pat. 127609, 1917. Rideal and Taylor, *Analyst*, **44**, 89 (1919). Rideal, *J. Chem. Soc.*, **115**, 993 (1919). Lamb, Scalione, and Edgar, *J. Am. Chem. Soc.*, **44**, 738 (1922).

[3] *J. Am. Chem. Soc.*, **43**, 1273 (1921).

[4] *J. Am. Chem. Soc.*, **45**, 920 (1923).

[5] Cf. Taylor, *J. Franklin Inst.*, **197**, 1 (1922).

is uncertain whether in the earlier work the walls of the vessel acted catalytically; also, the abnormal temperature coefficient obtained by Bodenstein, 1.34, between 234° and 283° C. and 1.77 between 310° and 356° C. does not seem to be in harmony with Bodenstein's conclusion that the reaction is homogeneous and confined to the gas phase.

Norrish and Rideal, by employing a dynamic method, have found it possible to show that the combination of hydrogen and sulphur takes place by way of two reactions, a gaseous and a surface reaction, the former being predominant, under the conditions of their experiments, at 285° C. and upwards, the latter being the more important below this temperature. They have shown, also, that the temperature coefficients of the two separate reactions were constant but widely different in value.

These conclusions were reached by an analysis of the reaction velocity measurements. They revealed that the logarithms of the total reaction velocity plotted against temperature did not yield straight lines. The curves obtained confirmed Bodenstein's result of an increasing temperature coefficient with increasing temperature. From measurements at different temperatures with two different hydrogen pressures, p_1 and p_2, it was found that a plot of the logarithms of the differences of corresponding velocities for the two pressures against temperature gave a straight line. This fact led the authors to the conclusion that a surface reaction and a gas reaction were proceeding concurrently and that the former, assumed independent of the gas pressure and therefore constant, disappeared on taking the difference of the corresponding velocities. In other words, the straight line obtained as stated is in reality the graph of the gas reaction velocity occurring at pressure $p_1 - p_2$. Assuming that the gas reaction velocity was proportional to the pressure and the surface reaction independent of the gas pressure, the observed curve for total reaction was resolved into two straight line curves of logarithm of velocity plotted against temperature for the two reactions taken separately. From the slope of these lines the temperature coefficients were obtained. That for the surface reaction was found to be 1.48, that for the gaseous reaction was 2.26 which, after correcting for the variation of the vapor pressure of sulphur with the temperature, reduced to 2.19. Corresponding to these coefficients, by applying the Arrhenius equation,

$$\frac{d \log V}{dT} = \frac{A}{RT^2},$$

where V is the reaction velocity, the values of A, the heats of activation of the gaseous and surface reactions, were found to be respectively 52,400 and 26,200 calories. Norrish and Rideal call especial attention to the fact that these are in the ratio 2 : 1.

By varying the size of the reaction vessel they showed also that the surface reaction was directly proportional to the internal surface area of the vessel and independent of the quantity of sulphur in the bulb. The respective

reaction equations would therefore be:

$$V_{\text{gas}} = k_1 \times C_{H_2} \times C_S,$$
$$V_{\text{surface}} = k_2 \times \text{Surface area},$$

where C_{H_2} refers to the hydrogen concentration, C_S that of the monatomic sulphur.

Norrish and Rideal [1] showed also that oxygen functions catalytically in the union of hydrogen and liquid sulphur. The phenomenon is in reality quite complex. With rise of temperature and increase of oxygen concentration, beyond 10 per cent at a temperature of 265° C. and beyond 7 per cent at 285° C., the catalytic action becomes a poisoning action. The observed effects were separated into a strong poisoning effect in the gaseous reaction between hydrogen and sulphur at all temperatures and a catalytic effect on the surface reaction which only becomes observable at the lower temperatures (265° and 285° C.) where the surface reaction is of greater relative importance. This surface catalytic action rises to a maximum with increase of oxygen concentration in the hydrogen and then falls away again, finally becoming a poisoning action for concentrations of oxygen beyond 10 per cent. Simultaneously, sulphur dioxide is formed at a rate directly proportional to the oxygen concentration.

From the known velocities of the several reactions occurring, it was deduced that the effects observed may be quantitatively explained by postulating a gradual preferential adsorption of oxygen by the sulphur surface, all the hydrogen being displaced when the gaseous concentration of oxygen has exceeded 10 per cent, and by ascribing to the oxygen a catalytic activity proportional to the number of molecules adsorbed per square centimeter of surface. From these assumptions Norrish and Rideal calculate the composition of the adsorbed gas films in equilibrium with a given atmosphere. It is evident from this work and that of Pease [2] that experimental determinations of such adsorptions from mixtures would be instructive.

In a concluding section of the paper Norrish and Rideal consider the mechanism of both gaseous and surface reactions. The thermal value found from the temperature coefficient of the gaseous reaction, the "critical increment" of the radiation theory, 52,400 cals., is in agreement with Budde's value [3] for the heat of dissociation of S_2 molecules into atoms, and thus corresponds to the energy required to sever two sulphur bonds. The critical increment of the surface reaction similarly corresponds to the breaking of one sulphur bond and is equal to that required to sublime a molecule of S_2 from the surface, which also involves the breaking of one bond. The surface reaction is considered to take place in two stages: (1) adsorption of the molecule, involving the breaking of one bond and (2) removal of the molecule of hydrogen sulphide, involving breaking of the second bond, the critical increment measured corre-

[1] *J. Chem. Soc.*, **123**, 1689 (1923).
[2] *J. Am. Chem. Soc.*, **45**, 1196, 2235, 2296 (1923).
[3] *Z. anorg. Chem.*, **58**, 169 (1912).

sponding to the slower of the two processes. The authors also assume that the surface contains mainly S_8 molecules of which a few are opened by the rupture of a linkage and thus polarized. The adsorption of the hydrogen and the oxygen is assumed to occur at these positions. The catalytic effect of the oxygen is attributed to simultaneous adsorption of oxygen and hydrogen at the two ends of the ruptured S_8 molecule. The strong attraction of the oxygen for the sulphur at one end of the chain will cause a weakening of the force by which the sulphur is held at the other end and thus lower the critical increment of energy necessary to remove the end sulphur atom as hydrogen sulphide.

More recently the authors have reached the conclusion that the activation of sulphur molecules is a quantum process and that the critical increment of 52,000 cals. corresponds to the absorption of a quantum of frequency of light whose wave-length is $\lambda = 2750$ Å. They have shown that the gas reaction between hydrogen and sulphur is markedly accelerated by ultra-violet light of this frequency.

The Rate of Solution of Gases in Liquids: The literature of reaction velocity measurements on the solution of gases in absorbing liquids is relatively scanty, although the problem is of importance not only theoretically but also as governing the design of gas scrubbing towers for a variety of purposes. Donnan and Irvine Masson [1] in a recent contribution to the theory of gas scrubbers have reviewed this literature. They call attention to the pioneering work of Hurter,[2] who studied in detail the important factor of the area of gas-liquid interface offered per unit of volume of gas per unit of time; on this basis Hurter discusses the relative advantages of bubbling, spraying and tower-packing. Renewed interest has been manifested in the subject recently, more especially in the direction of determining the effect of the solubilities and other specific properties of the gases and of the liquids which may be employed.

Adeney and Becker have studied [3] the rate of solution of air, oxygen and nitrogen in contact with quiescent de-aërated water and when a bubble of the gas in question is rising through a column of such water. The saturation of a quiescent de-aërated water with air has been commonly assumed to occur in two stages: (*a*) a rapid process of saturation of the surface layer under the prevailing conditions and (*b*) a slow process of diffusion of the dissolved gases through the mass of the water below the surface layer.[4] Adeney [5] had already shown that the second stage is not a simple diffusion process, but that the dissolved gases are gravitationally drawn downwards through the lower layers of the water with comparative rapidity. Temperature and temperature changes, salinity of the water, humidity of the air, depth of water, and other factors profoundly influence the rate of the solution process by such quiescent layers.

[1] *J. Soc. Chem. Ind.*, **39**, 236, T (1920).
[2] *J. Soc. Chem. Ind.*, **4**, 639 (1885); **6**, 707 (1887); **8**, 861 (1889); **12**, 227, 789 (1893).
[3] *Proc. Roy. Dublin Soc.*, **15**, 385, 609 (1918); **16**, 143 (1920).
[4] Ostwald, Solutions, p. 10.
[5] *Trans. Roy. Dub. Soc.*, 1914. *Phil. Mag.*, **9**, 360 (1905).

With moving bubbles of air in water, when the water was kept thoroughly mixed and the water-air surface unbroken, Adeney and Becker showed that the rate of solution took place in accordance with the general equation

$$\frac{dw}{dt} = a - bw,$$

in which a represents the initial rate of solution and bw the rate of escape of the gas from the water, b being a constant depending on the experimental conditions. The method of experimentation consisted in enclosing a large bubble of air, of known volume, in a narrow tube containing de-aërated water, and allowing the bubble to pass up through the water repeatedly until saturation was reached. The pressure in the bubble was measured after each double passage up the tube by means of a water manometer. From the observed pressure the absorption taking place could be calculated.

By extending these observations to different sizes of bubbles in a given tube and by a study of the influence of temperature on the process, Adeney and Becker were able to show that the above equation could be resolved into terms dependent on the bubble area and volume, the gas pressure and the concentration of dissolved gas. The equation so derived is:

$$\frac{dw}{dt} = SAp - f\frac{A}{V}w,$$

where S is the initial rate of solution per unit area, f is the coefficient of escape from the liquid per unit area and volume, A is the surface area, V the liquid volume, p the gas pressure and w the weight of gas dissolved. The significance of this expression is evident at the saturation state, when dw/dt is equal to zero For, then

$$SAp = f\frac{A}{V}w,$$

or, since $\frac{w}{V} = c$, the solute concentration,

$$Sp = fc,$$

or

$$\frac{c}{p} = \frac{S}{f} = k.$$

Hence, $S/f = k$, the coefficient connecting pressure and concentration for a gas obeying Henry's Law.

One other feature of interest can be drawn from the above equation of Adeney and Becker. When the values of f for any gas are multiplied by the solubilities, the product gives the initial rate of solutions, since

$$S = f \times s,$$

s being the solubility. The experimental results show that S is practically a

constant over a range of 30 degrees Centigrade for each gas. For different gases S varies approximately as the solubility.

For a constant area of interface Adeney and Becker's results may therefore be expressed, as pointed out by Donnan and Masson, by an equation of the form

$$\frac{dw}{dt} = k_2(km - n),$$

where m is the concentration of absorbable component in a gas phase, n the corresponding concentration in the liquid, k is the Henry's Law coefficient

$$n = km$$

and k_2 may be termed the dissolution coefficient. The equation is in this form only applicable to gas-liquid systems obeying Henry's Law and is an expression of the fact that the rate of solution at any moment is proportional to the unsaturation of the liquid at that moment.

By studying the effect of bubble area on the rate of solution, Adeney and Becker established that different portions of the approximately cylindrical bubbles had different effective solution rates on the gas. It was deduced that the conditions holding for the cylindrical sides of the bubble did not hold for the hemispherical head. The rate at which the water streams past the head of the bubble is less than that at which it passes down the cylindrical portion of it; hence, the absorption due to the head of the bubble is greater than might be expected from its area. By using different bubble volumes, varying the ratio of cylinder area to hemispherical head, this factor could be corrected for and apparent effective areas employed in place of the observed bubble areas. This observation emphasizes the dependence of absorption rate on the dynamics of the gas and liquid.

For cases in which Henry's Law does not hold, Donnan and Masson suggest an equation of the form

$$\frac{dw}{dt} = k_2(f(m) - n),$$

where the equilibrium isotherm has the form

$$n = f(m).$$

Under strictly specified conditions the dissolution coefficient, k_2, will be a constant quantity, but, in general, its value will increase with the degree of relative motion of gas and liquid and the degree of turbulence in both. The part played by the very thin "stagnant layer" in hindering the exchange of heat energy or of matter between different phases is well known to be a decisive factor in the design of heat interchangers and recuperators, furnaces, dissolvers, extractors and the like, and the thickness of this layer is diminished by the increase of relative motion of the phases and by rupture of this layer due to the splashing of drops. The term k_2 is therefore a dynamical coefficient.

It is apparent that the term $(km - n)$ in the Donnan-Masson expression is a potential factor expressing the driving force determining the magnitude of the absorption. It may be expressed by a slight rearrangement in the form

$$\text{Driving potential} = c_g - c_l,$$

where c_g is the concentration of the solute in the gas phase and c_l the corresponding concentration in the liquid phase. In the work of W. K. Lewis [1] and his associates [2] another expression for this driving potential has been employed. Instead of the concentrations, the partial pressures of the solute in the two phases have been substituted, the expression becoming

$$\text{Driving potential} = p_g - p_l.$$

It is evident that, for absorption at constant temperature, using a solute which obeys Henry's Law, i.e., $p = kc$, the two formulæ are identical. For, under these conditions,

$$(p_g - p_l) = k'(c_g - c_l).$$

The constant K_p connecting rate of absorption with driving potential employing pressures would be related to that connecting rate with driving potential employing concentration, K_c, by the expression

$$\frac{K_c}{K_p} = k',$$

since, on the several assumptions,

$$\frac{dw}{dt} = K_p(p_g - p_l) = K_c(c_g - c_l).$$

Whitman [3] has examined the physical significance of these two expressions. The equation employing pressures implies a concept picturing diffusion through a gas film, actuated by a difference in the partial pressure of the solute at the outside of the film (in the main body of the gas) and the inside of the film (in equilibrium with the liquid). The other concept considers diffusion through a liquid film on the surface of the main body of the liquid with diffusion controlled by a difference in concentration between the outside of the film (in equilibrium with the gas) and the interior of the liquid (the true liquid concentration).

From information obtained in a study [4] of humidification and de-humidification, Whitman has been led to the conclusion that two stationary films, gas and liquid, are involved in such processes and in gas-absorption processes in general. He concludes from the experimental data that the relative importance of the two films varies with the experimental conditions. In humidification

[1] *J. Ind. Eng. Chem.*, **8**, 825 (1916).
[2] Whitman and Keats, *ibid.*, **14**, 185 (1922).
[3] *Chem. Met. Eng.*, **29**, 146 (1923).
[4] Whitman and Keats, *J. Ind. Eng. Chem.*, **14**, 185 (1922).

processes the liquid film resistance is eliminated. In certain de-humidification experiments it amounted to 75 per cent of the total. Furthermore, the effect of such variables as liquid and gas velocities on the resistances of the separate films differed to a considerable extent. Whitman has therefore examined the implications of the dual film theory in processes of gas absorption.



FIG. 4

He assumes a stationary gas film on the upper side and a stationary liquid film on the lower side of a horizontal surface of contact between a gas and a liquid as indicated in Fig. 4. He points out that diffusion through the gas film should be determined by a partial pressure gradient, $p_1 - p_2$, of the solute and that diffusion through the liquid film should be determined by a concentration gradient $c_2 - c_3$. On such an assumption Whitman deduces the following expression for the rate of absorption:

$$\frac{dw}{dt} = k_p(p_1 - p_2) = k_c(c_2 - c_3),$$

where k_p is the coefficient of diffusion through the gas films and k_c is the coefficient of diffusion through the liquid film. The values of k_p and k_c will depend on the experimental conditions.

The essential distinction between these equations and those previously developed, which, expressed on the two-film basis, become

$$\frac{dw}{dt} = K_p(p_1 - p_3)$$

and

$$\frac{dw}{dt} = K_c(c_1 - c_3),$$

is that in the older equations K_p and K_c are overall coefficients from state 1 to state 3; they can only have broad application when the concentration is directly proportional to the pressure. If the deviations from Henry's Law are considerable, or if the temperature range under consideration is considerable, overall coefficients would have little or no significance.

Whitman attempts to test the two-film theory by experiments on the rate of absorption of hydrogen chloride in various strengths of aqueous solutions of hydrochloric acid at 30° C. Several factors governed this choice. Henry's Law is not fulfilled by the system. For acid concentrations up to 250 grams per liter the partial pressure of hydrogen chloride is negligible. Hence, it follows that, with acids the surface concentrations of which are below this figure, the gas will be absorbed as rapidly as it reaches the surface. The equation becomes

$$\frac{dw}{dt} = K_p \cdot p_1.$$

Furthermore, K_p is identical with k_p in this case.

At higher concentrations of acid, however, the equilibrium pressure on the surface becomes relatively large [1] and also changes rapidly with concentration. Consequently, the absorption of a small amount into the surface brings this into substantial equilibrium with the gas, thereby preventing further absorption until the absorbed acid has diffused through the liquid film into the interior. The available concentration gradient is slight and consequently the rate of diffusion is slow. This would account for the well-recognized fact that for the same pressure gradient the rate of absorption into the dilute towers of a hydrochloric acid system is far more rapid than in those towers containing strong acid. The data obtained by Whitman are presented in Table XVI.

TABLE XVI

ABSORPTION OF HYDROGEN CHLORIDE

Run	$\frac{dw}{dt}$	p_1	p_3	p	C_1	C_3	C	K_p	K_c
		mm. Hg			g. per liter				
1	41.0	225	55	170	425	378	47	0.24	0.87
2.....	24.0	41	0.3	40.7	368	204	164	0.59	0.146
3.....	24.1	41	0.0	41.0	368	9	359	0.59	0.067

The data show that neither K_p nor K_c, the overall coefficients, are constant. It will be noted that the second and third values for K_p are constant though those for K_c differ more than twofold: The conditions of these runs represent a specific limiting case where the pressure potential alone is a sufficient consideration. It is to be noted that p_3 in each of these cases is very small.

The data can be treated on the basis of the two-film theory. Thus, since

$$\frac{k_c}{k_p} = \frac{p_1 - p_2}{c_2 - c_3} \qquad \text{and} \qquad \frac{K_p}{k_p} = \frac{p_1 - p_2}{p_1 - p_3}$$

and assuming that $K_p = k_p = 0.59$ from Run 3, where the absorbing liquid is so dilute that the pressure p_2 is practically zero, we can calculate the value of k_c from the data of Run 1. Thus,

$$\frac{K_p}{k_p} = \frac{0.24}{0.59} = \frac{225 - p_2}{225 - 55},$$

whence,

$$p_2 = 156 \text{ mm.}$$

The corresponding concentration $c_2 = 412$ grams per liter as calculated from vapor pressure data. The constant, k_c, becomes therefore

$$k_c = \frac{w/t}{(c_2 - c_3)} = \frac{41.0}{412 - 378} = 1.2.$$

[1] Dolezalek, *Z. physik. Chem.*, **26**, 334 (1898). Bates and Kirschbaum, *J. Am. Chem. Soc.*, **41**, 1897 (1919).

It is possible to check this value for k_c in the data of Run 2. Thus,

$$\frac{k_c}{k_p} = \frac{1.2}{0.59} = \frac{p_1 - p_2}{c_2 - c_3} = \frac{41 - p_2}{c_2 - 204}.$$

From the vapor pressure data the values for p_2 and c_2 which satisfy this equation are found to be $p_2 = 0.6$ mm. and $c_2 = 224$ grams per liter. Hence

$$\frac{dw}{dt} = k_c(c_2 - c_3) = 1.2(224 - 204) = 24 \text{ grams per hour},$$

a value in good agreement with experiment.

This experiment constitutes, as yet, the sole published evidence in support of the two-film theory. Further work is promised and is much to be desired. For, it is evident that the concept of a gas film of the nature indicated in this treatment is not in harmony with so much of the treatment found valid by Langmuir in the case of reactions at solid surfaces. On Langmuir's method of treatment there should be no gas film of the nature postulated by Whitman. A unimolecular layer of adsorbed molecules would represent the maximum film which could be formed. That the application of Langmuir's unimolecular hypothesis to liquids is not without experimental basis is evident from the recent researches of Iredale [1] on the adsorption of methyl acetate vapor on the surface of mercury droplets, the extent of adsorption being measured by the change in surface tension of the mercury. Iredale found a rapid change in surface tension as the pressure of methyl acetate increased to 62 mm. beyond which it remained constant until the saturation pressure of methyl acetate, 225 mm., at the given temperature, 26° C., was reached. At that pressure the surface tension changes suddenly to that of mercury in methyl acetate. Calculation by means of the Gibbs adsorption isotherm at the pressure of 62 mm. showed the mercury droplets to be covered with a single layer of methyl acetate molecules of the same cross-sectional area as was obtained by Langmuir from his oil film experiments on water surfaces for the area occupied by a fatty ester molecule in the films.

For all processes composite of two separate stages, as in this present case, it is to be remembered that the net tempo of the process *at the steady state* is governed by that of the slower stage. Before the steady state is reached, however, the rate of the process will be determined by the rate of the initial stage in the process. In the problem under consideration it is evident that the initial process in the absorption is the diffusion of the absorbable gas to the gas-liquid interface and this, from the densities of the two media concerned, would certainly be more rapid than the removal of the dissolved molecules from the interface into the solution. One would expect, therefore, that a method of ascertaining the rate of absorption of a gas which could record rates sufficiently rapidly should reveal initial high absorption rates followed by a continuous fall until a steady state is reached.

[1] *Phil. Mag.*, **45**, 1088 (1923).

A method capable of recording rates of absorption of gases from gas bubbles over minute intervals of time from the moment of formation of the bubble has recently been employed by Ledig and Weaver.[1] These authors have determined the rate of absorption of carbon dioxide from bubbles formed in water, in sodium hydroxide, sodium carbonate and cane sugar solutions. The method used is very simple in principle. A bubble of the gas is absorbed in a system open to the air only through a capillary tube. The resulting contraction of the bubble produces motion in the thread of solution in the capillary tube. A photographic method is used to obtain a time record of this motion, the timing being secured by a 54-cycle electrical tuning-fork which opens and shuts a slit, records of the openings being thus secured on one edge of the moving paper employed to register the motion of the thread of solution.

The results obtained in this study can best be seen in the absorption curves for very dilute solutions shown in the accompanying Fig. 5. The absorption

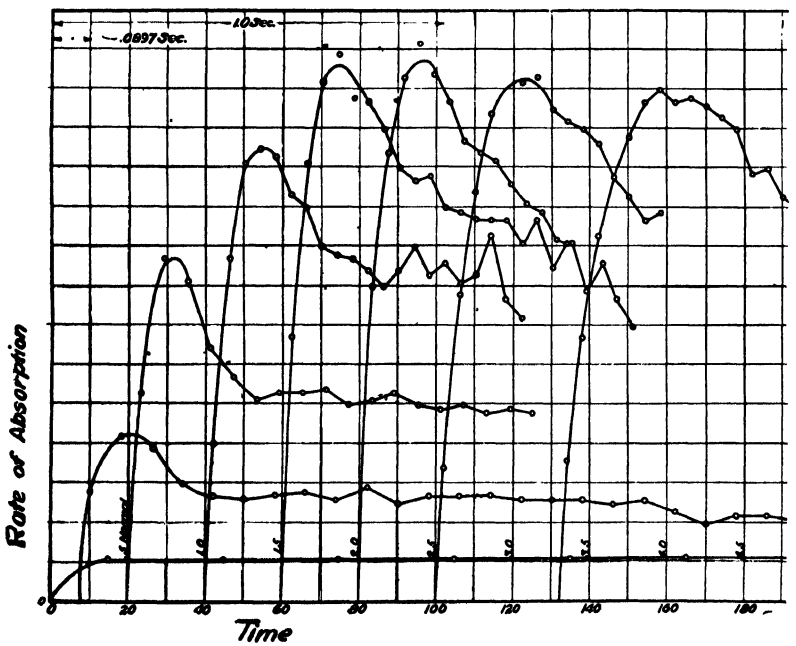


FIG. 5. Absorption of Carbon dioxide by Sodium Hydroxide Solutions

follows a three-stage cycle. The curve is begun by a *very high absorption rate* at the newly-formed liquid-gas surface, but as absorption goes on it falls again very quickly to a rate where an equilibrium condition exists. The authors state that this rate is controlled by the diffusion of the reagent to the surface and of the reaction product away from the surface. On the view expressed

[1] *J. Am. Chem. Soc.*, **46**, 650 (1924).

above it is this latter factor which is operative. The third stage in the cycle begins, in the view of the authors of the method, when the diluting gas starts to slow up diffusion of the gas to the surface, though they point out that it is undoubtedly considerably affected by the diminished buoyancy or rate of rising; as the bubble becomes smaller there is, accordingly, a decrease in the stirring action which renews the absorbing liquid around the bubble.[1]

The curves shown are rates of absorption plotted against time, though the initial points of the curves are arranged to show the concentration relations of the solutions of sodium hydroxide used. The fact that the rate does not rise instantaneously to the maximum can be attributed in part to three factors: (1) the bubble breaks out of the mercury (in which it is formed) during a measurable period of time rather than instantaneously; (2) the inertia of the liquid in the capillary tube and surface tension at the free meniscus require a definite pressure difference caused by absorption to produce motion; and (3) the viscosity of the solution itself produces a lag in the rise to the maximum. These factors seem sufficient to account for the time (about 0.1 sec.) required to reach a maximum rate in the case of the dilute solutions. The theoretical shape of these curves would therefore be maximum initial absorption rate (corresponding to gaseous diffusion and condensation on the surface) followed by a decrease to a steady rate, this latter corresponding to removal of solute from the interface into the solution. With the more concentrated solutions, as much as 0.75 second is required to attain the maximum rate. This must involve some additional factor which has not been fully explained. It is noteworthy that it occurs with sodium hydroxide solutions whose conductivity is less than the maximum conductivity given by more dilute (2 normal) solutions. Viscosity may be one of the factors contributing to this delayed maximum.

The diagram already cited and that reproduced below, Fig. 6, show that with water as absorbent, Curve 1, no initial high values are obtained. This would indicate very rapid saturation of the surface when no absorbing agent is present, certainly within the interval (0.1 sec.) in which initial disturbances are present. It is to be noted from the former figure that, with increasing strength of sodium hydroxide solutions up to 2.0 normal, the initial rate successively increases. Curves 2 and 3 reproduce absorption rates with aqueous cane sugar solution and 2.5 normal sodium carbonate solution. The cane sugar solution was of such a concentration that it had the same viscosity as the sodium carbonate solution. It is evident that sodium carbonate depresses the rate of solution even more than can be accounted for on the basis of the viscosity of the liquid medium. The authors assume the difference to be due probably "to the mass-action effect of the carbonate and bicarbonate ions in solution." On the assumption that the steady state is determined by the diffusion process in the liquid medium, another possible explanation is forth-

[1] Even in case the carbon dioxide introduced into the solution is pure, some other gas (e.g., dissolved air) will diffuse into the bubble while it is still large and will become apparent when the size is considerably reduced.

coming. In the one case the solute diffusing will be hydrogen ions and carbonate ions, in the other sodium, hydrogen and carbonate ions. For reasons given in the earlier sections of this chapter, since the diffusion coefficient of an electrolyte is given (page 937) by the equation,

$$D = \frac{UV}{U + V} RT,$$

the acid ions would be expected to wander into the interior of the solution more rapidly than the ions of the acid salt.

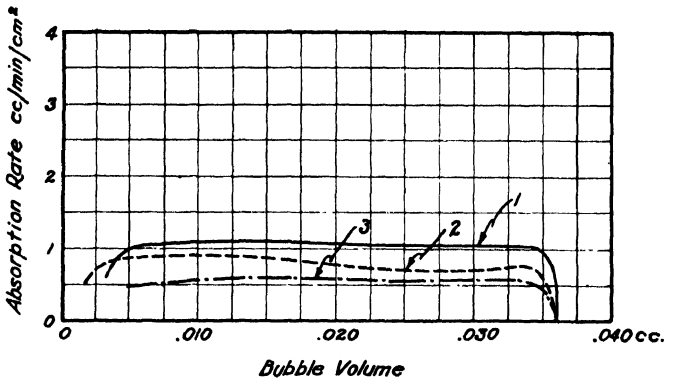


FIG. 6. Absorption of Carbon Dioxide by Water, Aqueous Cane Sugar and Sodium Carbonate Solutions.

Ledig and Weaver state that this is the first part of a general investigation of the rates of solution of gases in liquids. The study of numerous additional examples is especially to be desired. A study of the absorption of hydrogen chloride bubbles in water and aqueous hydrochloric acid solutions would be highly interesting, probably decisive as a test of the several points of view herein set forth. A knowledge of the effect of temperature would also assist in the understanding of the mechanism. Until such data are forthcoming the speculative nature of much of this present section on the rate of absorption of gases in liquids should be borne in mind.

CHAPTER XVI

THE QUANTUM THEORY IN PHYSICAL CHEMISTRY

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The quantum theory originated in an attempt to account for certain phenomena in the emission and absorption of radiant energy. It presents us with an atomistic view of energy transformations that is totally at variance with the undulatory theory as formulated by Huygens and extensively developed by Clerk Maxwell into the electromagnetic theory of radiation. In spite of many efforts to the contrary, the quantum theory has up to the present been found to be the only reasonable hypothesis by which a large number of observations can be correlated. These observations, which admit of no explanation in terms of the classical theory, are in fact logically opposed to the deductions of this theory and yet they are among the most striking that have been discovered in the whole history of physics and chemistry. The influence of this new point of view on the development of physical chemistry during the past decade has been profound. Our whole conception of atomic structure, of the mechanism of chemical and physical reaction, of the significance of the laws of thermodynamics—all our previous ideas on these subjects have been completely revolutionized through the application of the quantum theory. Indeed, just as in the past we have had in the history of chemistry the period of the phlogiston theory, that of the dualistic hypothesis and so forth, so the historian of the future will undoubtedly be justified in designating the present as the "Period of the Quantum Theory."

Classical Theory of Energy Radiation: To understand the nature of the facts which have led to the development of the quantum theory, it is necessary to consider briefly the fundamental observations upon which the classical or wave-theory of electromagnetic radiation is founded. As summarized by R. A. Millikan [1] these are as follows: (1) the facts of interference of light, (2) the fact that the speed of light is greater in air than in water, (3) the discovery of wireless waves, (4) the observation that the speed of light is independent of the velocity of the source.

By the end of the nineteenth century this theory was apparently firmly entrenched. It was universally accepted that energy is propagated in space continuously by means of spreading wave-fronts and that this propagation is adequately and sufficiently represented by the electrodynamical equations of Maxwell. The doctrine was held that "nature takes no leaps"—*natura non*

[1] Radiation and the Electron, *J. Franklin Inst.*, **184**, 337 (1917).

saltus facit, and that all phenomena are governed by differential equations—that is, equations of continuity.

Origin of Quantum Theory: In 1901 there appeared a paper by M. Planck [1] in which he pointed out that the observations on the law of distribution of energy in black body radiation could not be reconciled with the classical point of view. He, therefore, formulated the hypothesis that energy may be emitted or absorbed discontinuously in multiples of a certain unit or *quantum* of magnitude $h\nu$, where ν is the frequency of the radiation and h is a universal constant (known as Planck's, or the quantum constant).

The arguments upon which Planck based his conclusions and theory are not very easy to follow so that we shall postpone the discussion of these considerations for a subsequent section. This is made possible by the fact that many other observations have been made since 1900 which lead to a quantum hypothesis in such an obvious manner that it is not necessary to follow the historical development in order to understand the new point of view.

Ionization and Electron Ejection by X-Rays: One of the first observations which threw doubt on the universal validity of the wave-theory of light concerns the ionization of atoms by X-rays. As we know from the investigations of Laue, Bragg and others, X-rays are propagated in space in the same manner as ordinary electromagnetic energy. But while, for instance, the visible radiation ranges in wave-length from approximately 3600 to 7700 $\times 10^{-8}$ cm., the wave-lengths of X-rays lie between 100 and 0.1 $\times 10^{-8}$ cm. approximately. Now it was observed that, when X-rays pass through a gas, they ionize only about one in a thousand billion of the molecules or atoms which are actually in the path of the rays. Apparently, the X-rays do not lose any energy whatever for quite a distance, while they pass over billions of molecules, and then, for some unknown reason, one molecule absorbs the energy of a whole train of X-ray waves and an electron is ejected (this constitutes the process of ionization). Furthermore, the velocity with which the electron is ejected bears a very simple relation to the frequency of the X-rays. If v denote the velocity, and m the mass of the electron, while ν denotes the frequency of the (monochromatic) X-rays, it is found that

$$\tfrac{1}{2}mv^2 = h\nu. \qquad (1)$$

That is, the energy of the electron is equal to the frequency of the radiation multiplied by Planck's constant.[2] Similarly, when X-rays impinge on a solid body, electrons are emitted with maximum velocities, which are related to the frequency of the radiation by the same equation. The number of electrons emitted depends, however, on the intensity of the incident radiation.

These observations are quite unexpected from the point of view of the ordinary wave-theory of radiation. According to the latter theory, the energy per unit area of wave-front decreases continually as the waves spread out more and more. Yet, the X-rays are able to retain their original energy unimpaired

[1] M. Planck, *Ann. Physik*, **4**, 553 (1901).

[2] A. Einstein, Ann. Physik, **17**, 132 (1905); **20**, 199 (1906).

for a considerable distance; they can pass over an enormous number of molecules, and then concentrate the whole of the energy into the ejection of an electron from some one molecule.

Relation between Frequency of X-Rays and Velocity of Electrons: The converse of the above process also occurs. If we direct a stream of electrons against any solid, X-rays are obtained, and it has been known for a number of years that the "hardness" of the rays increases with the voltage applied to the X-ray tube. The velocity which the electrons acquire in passing from cathode to anode is given by the relation

$$\tfrac{1}{2}mv^2 = Ve,^1 \tag{2}$$

where V denotes the voltage between the electrodes and e the charge on the electron.

The X-radiation produced by the incidence of the electrons on the anode (or target) presents a continuous spectrum in which the intensity varies in a complicated manner with the wave-length. Fig. 1 [2] shows the spectra obtained at five different voltages from 20,000 to 40,000 volts, with a Coolidge X-ray tube containing a tungsten anode. It will be observed that the intensity is very low for longer wave-lengths, increases with decrease in wave-length to a maximum value and then decreases rapidly to zero at a certain well-defined wave-length. At higher voltages there are superposed upon this continuous spectrum one or more peaks whose intensity is considerably greater than that of the general radiation.

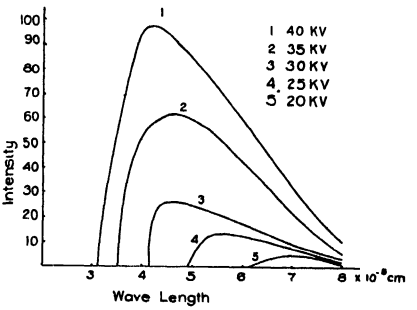


FIG. 1. Variation of Intensity with Wave-length of X-rays

These peaks indicate what are known as the characteristic X-rays, the wave-lengths of which depend upon the nature of the anode material. While these radiations also present certain interesting features from the point of view of the quantum theory, the remarkable feature about the continuous spectra is the fact that the minimum wave-length ($\lambda_{min.}$) or maximum frequency ($\nu_{max.}$) depends upon the applied potential difference V in accordance with the relation

$$Ve = h\nu_{max.} = \frac{hc}{\lambda_{min.}} . \tag{3}$$

[1] It must be observed that, on the basis of the Theory of Relativity, m, the mass of the electron, increases with the velocity according to the relation

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}},$$

where c = velocity of light and m_0 = mass at very low velocities.

[2] Fig 1 is Fig. 7 of A. W. Hull's paper on Roentgen Ray Spectra, *Am. J. Roentgenology*, Dec., 1915.

That is, there exists a linear relation between the kinetic energy of the electrons and the maximum frequency of the resulting X-radiation. The proportionality constant is again the quantum constant h. The validity of this relation has been tested by a number of observers and Table I gives values of h determined in this manner.

TABLE I[1]

Observers	Max. V	$h \times 10^{27}$ (erg. sec.)
Duane and Hunt[2]	40,000	6.51
Hull[3]	110,000	6.59
D. L. Webster[4]	44,000	6.53
Blake and Duane[5]	42,000	6.555
Müller[6]	28,000	6.58
Wagner[7]	10,600	6.49

Photo-Electric Effect: The emission of electrons by X-radiation is only a particular instance of a more general phenomenon which has been known for a number of years as the *photo-electric effect.*[8]

When a negatively charged surface of a metal is illuminated by ultra-violet light, electrons are emitted. In the case of the alkali metals, the same effect is produced by visible light, but it has been observed that for each surface there exists a minimum frequency (ν_0) of radiation which is just capable of causing photo-electron emission. As the frequency of the incident (monochromatic) radiation is increased above this minimum value, the velocity of the ejected electrons increases continuously, while the number of electrons varies directly with the intensity of the illumination. On the basis of Planck's theory, Einstein concluded that the energy of the electrons must vary linearly with the frequency of the radiation,[9] according to the relation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - h\nu_0. \tag{4}$$

The similarity with equation (3) is evident. The quantity $h\nu$ measures the energy absorbed by the electron from the radiation, $h\nu_0$ is the work necessary to get the electron through the surface, and $\tfrac{1}{2}mv^2$ is the actual energy with which the electron is emitted. This energy may be measured by the product of the electronic charge e and the potential difference V which is required to retard the velocity to zero.

[1] This table is taken from the excellent summary by Wm. Duane, Data Relating to X-ray Spectra, *Bull. Nat. Res. Council*, **1**, 383 (1920). The values of h given are calculated on the basis $\epsilon = 4.774 \times 10^{-10}$ electrostatic units.

[2] *Phys. Rev.*, **6**, 166 (1915).

[3] *Ibid.*, **7**, 156 (1916).

[4] *Ibid.*, **7**, 599 (1916).

[5] *Ibid.*, **10**, 624 (1917).

[6] *Physik Z.*, **19**, 489 (1918).

[7] *Ann. Physik*, **57**, 401 (1918).

[8] For the most recent discussion of this subject and references to literature, see the summary by A. Ll. Hughes, *Bull. Nat. Res. Council*, **2**, Part 2, April, 1921.

[9] A. Einstein, *Ann. Physik*, **17**, 132 (1905); **20**, 199 (1906). See also R. A. Millikan, The Electron, p. 223, Univ. of Chicago Press (1918).

The frequency ν_0 is also known as the "photo-electric threshold" and may be expressed in terms of a potential difference V_0 according to the relation

$$V_0 e = h\nu_0.$$

Thus, V_0 corresponds to the "work function" for electrons passing through the surface.

Equation (4) has been tested by R. A. Millikan and his students for a number of metals over a wide range of frequencies.[1] These investigations have shown that, within the limits of experimental errors, for any photo-electrically active surface, the maximum retarding potential V increases linearly with the frequency ν of the incident radiation, and that the slope of this line is given by h/e. Table II gives values of h obtained in this manner by different observers, over a fairly wide range of frequencies of radiation.

TABLE II

Metal	Observers	$h \times 10^{27}$
Sodium	R. A. Millikan [2]	6.561
Lithium	R. A. Millikan	6.584
Magnesium	A. E. Henning and W. H. Kadesch [3]	6.45
Aluminum	A. E. Henning and W. H. Kadesch	6.41
Zinc	P. E. Sabine [4]	6.70
Cadium	P. E. Sabine	6.57
Copper	P. E. Sabine	6.68

It is important to realize that the magnitude of the energy quantum *varies with the frequency* of the radiation. As a result of a large number of determinations by different methods (which will be discussed in this chapter), the value of h accepted at present as most accurate is 6.554×10^{-27} erg. sec.[5]

On this basis we obtain values of $h\nu$ for different types of radiation which are given in Table III.

TABLE III

Type of Radiation	Mean Value of ν	$h\nu$ (erg)	$h\nu$ (calorie)
Wireless waves	10^5	6.554×10^{-22}	1.566×10^{-29}
Heat waves	3×10^{13}	19.66×10^{-14}	4.721×10^{-21}
Visible light	6×10^{14}	39.32×10^{-13}	9.399×10^{-20}
X-rays	3×10^{18}	1.966×10^{-8}	4.721×10^{-15}
Gamma rays	3×10^{19}	1.966×10^{-7}	4.721×10^{-14}

[1] R. A. Millikan, The Electron, Chapter X; *J. Franklin Inst.*, **184**, 337 (1917); also A. Ll. Hughes, *loc. cit.*

[2] *Phys. Rev.*, **7**, 18, 355 (1916).

[3] *Ibid.*, **8**, 209, 221 (1916).

[4] *Ibid.*, **9**, 260 (1917).

[5] R. T. Birge, *Phys. Rev.*, **14**, 361 (1919); R. Ladenburg, *Jahrb. Rad. Elektronik*, **17**, 93 (1920).

For purposes of comparison, it may be observed that the amount of energy corresponding to the *formation* of *1 molecule* of water vapor from its elements is 3.962×10^{-12} ergs ($= 9.47 \times 10^{-20}$ calorie).

Mechanism of Quantum Radiation: These observations regarding the relation between radiant energy and energy of motion of electrons are remarkable when we consider them in the light of the classical theory. Sir William Bragg's remarks on this point state the contradictions involved in the phenomena in a very lucid manner.[1]

"In order to realize," he writes, "the full significance of these extraordinary results, let us picture the double process as it occurs whenever we use an X-ray bulb. By the imposition of great electrical forces we hurl electrons in a stream across the bulb. One of these electrons, let us say, starts a wave where it falls. This action is quite unaffected by the presence of similar actions in the neighborhood, so that we can fix our minds upon this one electron, and the wave which it alone causes to arise. The wave spreads away, it passes through the walls of the bulb, through the air outside, and *somewhere or other in its path in one of the many atoms it passes over, an electron springs into existence, having the same speed as the original electron in the X-ray bulb.* The equality of the two speeds is not necessary to the significance of this extraordinary effect; it would have been just as wonderful if one speed had only been one half or one quarter or any reasonable fraction of the other. The equality is more an indication to us of how to look for an explanation than an additional difficulty to be overcome.

"Let me take an analogy. I drop a log of wood into the sea from a height, let us say, of 100 feet. A wave radiates away from where it falls. Here is the corpuscular radiation producing a wave. The wave spreads, its energy is more and more widely distributed, the ripples get less and less in height. At a short distance, a few hundred yards perhaps, the effect will apparently have disappeared. If the water were perfectly free from viscosity and there were no other causes to fritter away the energy of the waves, they would travel, let us say, 1000 miles. By which time the height of the ripples would be, as we can readily imagine, extremely small. Then, at some one point on its circumference, the ripple encounters a wooden ship. It may have encountered thousands of ships before that and nothing has happened, but in this one particular case the unexpected happens. One of the ship's timbers suddenly flies up in the air to exactly 100 feet, that is to say, if it got clear away from the ship without having to crash through parts of the rigging or something else of the structure. The problem is, where did the energy come from that shot this plank into the air, and why was its velocity so exactly related to that of the plank which was dropped into the water 1000 miles away? It is this problem that leaves us guessing.

"Shall we suppose that there was an explosive charge in the ship ready to go off, and that the ripple pulled the trigger. If we take this line of explanation, we have to arrange in some way that there are explosive charges of all varieties of strength, each one ready to go off when the right ripple comes along. The right ripple, it is to be remembered, is the one whose frequency multiplied by the constant factor is equal to the energy set free by the explosion. The ship carries about all these charges at all times, or at least there are a large number of ships each of which carries some of the charges, and externally the ships are exactly alike. Also we have to explain why, if we may drop our analogy and come back to the real thing, the ejected electron tends to start its career in the direction from which the wave came. This is a very marked effect when the waves are very short.

"Dropping the analogy, how do the electrons acquire their direction of movement from waves whose energy and momentum have become infinitesimally small at the spot where they are affected, unless the atom has a mechanism of the most complicated kind? And if the intervention of the atom is so important, why is it that in these effects a consequence of the intervention does not depend upon each atom itself—whether, for example, it is oxygen or copper or lead?

[1] Scientific Monthly, **14**, 153 (1922).

"We may try another line of explanation and suppose that the energy is actually transferred by the wave from the one electron to the other. If it is the atom which pulls the trigger and causes the transformation, then how does it happen that the whole of the energy collected by the wave at its origin can be delivered at one spot? Rayleigh has told us that an electron over which a wave is passing can collect the energy from an area round about it whose linear dimensions are of the order of the wave-length. But any explanation of this kind is entirely inadequate. Whatever process goes on, it is powerful enough on occasion to transfer the whole of the energy of the one electron to the other. Nor can there be any question of storing up energy for a long period of time until sufficient is acquired for the explosion. For it is not *difficult to show that when an X-ray bulb is started and its rays radiate out, the actual amount of energy which can be picked up by an atom a few feet away would not be sufficient for the ejected electron, though the tube were running for months; whereas we find the result to be instantaneous.*

"I think it is fair to say that in all optical questions concerned with the general distribution of energy from a radiating source the wave-theory is clearly a full explanation. It is only when we come to consider the movements of the electrons which both cause waves and are caused by them that we find ourselves at a loss for an explanation. *The effects are as if the energy were conveyed from place to place in entities, such as Newton's old corpuscular theory of light provides. This is the problem for which no satisfactory solution has been provided as yet;* that at least is how it seems to me."

The wave-theory thus meets with two difficulties in attempting to account for the ejection of electrons by X-rays and ordinary radiation. First, a wave-motion is defined by frequency and amplitude of vibration, while the electron emission is defined by the number and speed of the electrons. The relation between the two is very simple. The number of electrons is proportional to the amplitude of vibration, while the energy of ejection is proportional to the frequency. That the speed of the electron is independent of the intensity is an extraordinary result from the point of view of the wave-theory. The second difficulty encountered by the latter occurs when we attempt to account for the observation that the radiation can apparently pass over so many atoms and then cause ejection of an electron from some one atom at the very instant that the radiation strikes it. There is no time lag whatever; there is no opportunity for the atom to store up the energy for subsequent conversion into kinetic energy of the electron.

Such considerations led Einstein in 1905 to formulate a semi-corpuscular theory of quantum radiation. According to this theory the energy emitted by any radiator keeps together in bunches or quanta as it travels through space, the magnitude of each quantum being given by $h\nu$. Another form of the same hypothesis was suggested by Sir J. J. Thomson. He assumed that the ether possesses a fibrous structure and pictured "all electromagnetic energy as travelling along Faraday lines of force conceived of as actual strings extending through all space." [1] But there are very serious objections to both these theories. Not only the phenomena of interference are completely in contradiction with such views, but the fact that the electro-dynamical equations of Maxwell have been found to be in satisfactory agreement with all ordinary electromagnetic phenomena makes it apparently inconceivable that a "pill" theory can take the place of the classical wave-theory.

[1] R. A. Millikan, *J. Franklin Inst.*, **184**, 337 (1917).

Lenard has suggested that the incident radiation catalyzes, as it were, the ejection of the electron. If this were true, then the nature of the atom should make a difference—which is not the case. We must, therefore, conclude that the energy required to expel the electron from the atom originates in the radiation itself.

"When, however, we attempt to compute on the basis of a spreading wave-theory how much energy a corpuscle can receive from a given source of light, we find it difficult to find anything more than a very minute fraction of the amount which the corpuscle actually acquires.

"Thus, the total luminous energy falling per second from a standard candle on a square centimeter at a distance of 3 m. is 1 erg. Hence the amount falling per second on a body of the size of an atom, i.e., of cross-section 10^{-15} cm.^{2}, is 10^{-15} ergs, but the energy $h\nu$ with which a corpuscle is ejected by light of wave-length 500 $\mu\mu$ (millionths millimeter) is 4×10^{-12} ergs, or 4000 times as much. Since not a third of the incident energy is in wave-lengths shorter than 500 $\mu\mu$, a surface of sodium or lithium which is sensitive up to 500 $\mu\mu$ should require, even if all this energy were in one wave-length, which it is not, at least 12,000 seconds or 4 hours of illumination by a candle 3 m. away before any of its atoms could have received, all told, enough energy to discharge a corpuscle. Yet the corpuscle is observed to shoot out the instant the light is turned on. It is true that Lord Rayleigh has recently shown that an atom may conceivably absorb wave-energy from a region of the order of magnitude of the square of a wave-length of the incident light rather than of the order of its own cross-section. This in no way weakens, however, the cogency of the type of argument just presented, for it is only necessary to apply the same sort of analysis to the case of γ-rays, the wave-length of which is of the order of magnitude of an atomic diameter (10^{-8} cm.), and the difficulty is found still more pronounced. Thus Rutherford estimates that the total γ-ray energy radiated per second by one gramme of radium cannot possibly be more than 4.7×10^4 ergs. Hence at a distance of 100 meters, where the γ-rays from a gramme of radium would be easily detectable, the total γ-ray energy falling per second on a square millimeter of surface, the area of which is ten thousand billion times greater than that either of an atom or of a disc whose radius is a wave-length, would be $4.7 \times 10^4 \div 4\pi \times 10^{10} = 4 \times 10^{-7}$ ergs. This is very close to the energy with which β-rays are actually observed to be ejected by these γ-rays, the velocity of ejection being about nine tenths that of light. Although, then, it should take ten thousand billion seconds for the atom to gather in this much energy from the γ-rays, on the basis of classical theory, the β-ray is observed to be ejected with this energy as soon as the radium is put in place. This shows that if we are going to abandon the Thomson-Einstein hypothesis of localized energy, which is, of course, competent to satisfy these energy relations, there is no alternative but to assume that at some previous time the corpuscle had absorbed and stored up from light of this or other wave-length enough energy so that it needed but a minute at the time of the experiment to be able to be ejected from the atom with the energy $h\nu$."[1]

Whatever the interpretation of Einstein's relation, the observed facts lead to the conclusion that the emission of energy by an atom is a discontinuous or explosive process. The constant h is the "explosive constant, i.e., it is the unchanging ratio between the energy of emission and the frequency of incident light."

Quantum Theory of Radiation

Black-Body Radiation. As mentioned previously, the quantum theory was originally formulated by Planck in 1901 in order to account for the observations on the distribution of energy in the radiation from a black body. Careful

[1] R. A. Millikan, loc. cit.

measurements on the energy distribution had been made by O. Lummer and E. Pringsheim in the previous years (1879–99), but all attempts to bring these observations into accord with the deductions of classical dynamics ended in failure. For a proper understanding of the fundamental basis of the quantum theory it is, therefore, necessary to review briefly the nature of the actual experimental data and then discuss their theoretical significance.

The total energy radiated from any solid and the distribution of energy with wave-length depend in general not only upon the temperature, but also upon the nature of the radiating surface. However, at any temperature, the energy radiated is a maximum for a so-called black body or full radiator. This has the property that, for any monochromatic radiation of wave-length λ, the energy emitted per unit area at any temperature is equal to that absorbed. Some materials, such as lamp black, approach the ideal surface very closely, while platinum and white oxides possess low coefficients of emissivity. (By this coefficient is meant the ratio between energy emitted and that absorbed.) As was pointed out by Kirchhoff, it is possible to determine the laws of black-body radiation from observations on the energy radiated from an enclosure that is maintained at a definite temperature.

Such experiments were carried out during the years 1897–1901 by Lummer and Pringsheim. Their results are shown in Fig. 2. The ordinates correspond to the intensities or emissive powers and the abscissæ are wave-lengths. (1 μ = 10^{-4} cm.)

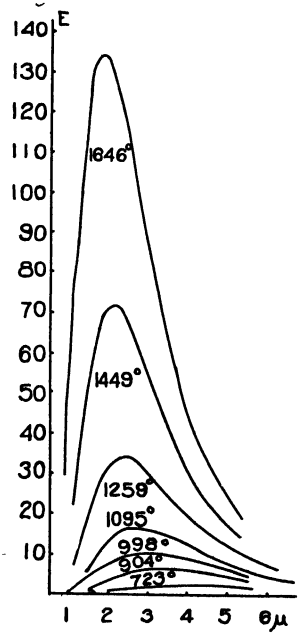


FIG. 2. Energy Distribution in the Spectrum

These curves show that at 723° K.,[1] the wave-length having the maximum energy is 4.08 μ, but there is sufficient energy even at 0.76 μ or slightly lower wave-lengths to affect the eye. Thus, a body at this temperature shows a red color. As the temperature increases above 723° K., the position of the maximum is continually shifted towards shorter wave-lengths until, at 1646° K., it is at wave-length 1.78 μ. At the same time, as the intensity of the energy in the shorter wave-lengths increases, the color of the radiation varies from red through cherry red and orange up to a bright white heat.

Intensity of Radiation: For the proper understanding of the laws of black-body radiation, it is necessary to examine further the physical significance of the energy distribution curves shown in Fig. 2.

Let us denote by E the total energy radiated per unit area per unit time by a full body radiator. This energy is composed of radiations of wave-

[1] Absolute temperatures will be designated by ° K. (Kelvin).

lengths varying from $\lambda = 0$ to $\lambda = \infty$. Furthermore, the intensity of each of these monochromatic radiations which constitute the total radiation is not the same. If we denote by E_λ the emissive power corresponding to wave-length λ, we obtain the obvious relation

$$E = \int_0^\infty E_\lambda d\lambda. \tag{1}$$

Thus, E_λ is the *differential-coefficient of E with respect to* λ. This is the physical significance of the ordinates used in Fig. 2. The total energy radiated at any temperature is given by the area under the corresponding distribution curve in this figure.

The infinitesimally small amount of energy $E_\lambda d\lambda$ represents the *energy flux* per unit area for a spectral region between λ and $\lambda + d\lambda$. Corresponding to this energy flux there exists a *specific intensity of radiation* of the surface, which we shall denote by K_λ, and it follows from very simple considerations that for unpolarized radiations

$$E_\lambda = 2\pi K_\lambda. \tag{2}$$

Thus K_λ designates the "brightness" of the surface, and in fact there is a similar relation between E_λ and K_λ as exists between the terms "lumens" and "candle-power" used in photometry.[1] The total lumens, L, emitted by a lamp having a mean hemispherical candle-power C is given by the relation

$$L = 2\pi C,$$

when we consider only the light emitted in one hemisphere. (On the other hand, the total lumens is $4\pi C$, where C corresponds to the mean spherical candle-power.)

If instead of the energy distribution curve with respect to wave-length we consider the distribution curve with respect to frequency, then

$$E = \int_\infty^0 E_\nu d\nu.$$

But

$$\nu = c/\lambda,$$

where c = velocity of light. Hence,

$$d\nu = -\frac{c}{\lambda^2} d\lambda \tag{3}$$

[1] K_λ may also be defined as follows: Consider an infinitesimally small surface from which the energy radiated at wave-length λ is $E_\lambda d\lambda$ per unit area and per unit time. Then, the energy passing per unit time through unit area at unit distance from the radiating surface is evidently $\frac{E_\lambda d\lambda}{2\pi}$, which corresponds to $K_\lambda d\lambda$.

In this connection it should be observed that in Planck's book the symbol E_λ is used with the same significance as K_λ in this chapter.

and

$$E_\lambda = \frac{c}{\lambda^2} E_\nu. \tag{4}$$

Also, corresponding to equation (2), we have

$$E_\nu = 2\pi K_\nu,$$

where K_ν designates the specific intensity of unpolarized monochromatic radiation of frequency ν.

Radiation Pressure and Energy Density: Since radiant energy is propagated in space with finite velocity, it is evident that there must be, in any given volume, a definite amount of energy, that is, there must exist a certain density of radiant energy, and this radiation in space must be in thermal equilibrium with the walls of the enclosure. A relatively simple calculation shows that the density u_ν of radiation of frequency ν is related to K_ν by the equation

$$u_\nu = \frac{8\pi}{c} K_\nu, \tag{5}$$

where c is the velocity of light.

The existence of radiation density necessarily leads to the conclusion that radiation must exert a pressure. For, energy per unit volume has the same dimensions as pressure per unit area. This theoretical deduction was actually confirmed by the experiments of Nichols and Hull.[1] According to the electromagnetic theory, the magnitude of the radiation pressure, p, corresponding to the energy density of the total radiation, u, at any temperature is given by

$$p = \frac{1}{3}\int_0^\infty u_\nu d\nu = \frac{u}{3}. \tag{6}$$

Evidently the last relation may also be expressed in terms of E, the total energy radiated, by the relation

$$p = \frac{4}{3c}\int_0^\infty E_\nu d\nu = \frac{4}{3c} E. \tag{7}$$

Stefan-Boltzmann Law: About 1879, Stefan concluded[2] from certain measurements of Tyndall that E, the total energy flux from a surface, varies with the fourth power of the absolute temperature. This relation is not true for any surface, but was subsequently deduced for black-body radiation by Boltzmann.[3] In his derivation, the latter made use of the fact that, corresponding to any temperature of a black-body enclosure, there exists a radiation

[1] *Phys. Rev.*, **13**, 293 (1901); **17**, 26, 91 (1903). *Ann. Physik*, **12**, 225 (1903).
[2] *Wien. Sitz. Ber.*, **79**, 391 (1879).
[3] *Wied. Ann.*, **22**, 33, 291, 616 (1884).

pressure of magnitude given by equation (7). By applying the second law of thermodynamics he then deduced the result

$$\left.\begin{aligned} E &= \sigma T^4 \\ \text{or} \qquad u &= \alpha T^4 \end{aligned}\right\} \tag{8}$$

where σ and α are constants. It follows from equation (7) that

$$\alpha = \frac{4}{c}\sigma. \tag{9}$$

Wien's Radiation Law: A further advance in the theoretical treatment of this subject was made by W. Wien [1] by assuming the following cycle:

Imagine the black-body enclosure filled with radiation at a certain temperature to be provided with a movable piston. The radiation will exert a pressure on the piston according to equation (6). We now perform a cyclic process in which the radiation is expanded adiabatically and then compressed very slowly. Taking into account the fact that, according to Doppler's principle, the color of any monochromatic radiation (that is, the frequency) is altered by reflection from a moving surface, and applying the second law of thermodynamics, it follows that

$$K_\nu = \frac{\nu^3}{c^2} F\left(\frac{\nu}{T}\right), \tag{10}$$

where the form of the function F still remains undetermined.

It was also deduced that, as the temperature increases, the frequency (ν_m) at which K_ν has the maximum value varies directly as the absolute temperature. That is,

$$\nu_m = \text{const.} \times T \tag{11a}$$

or

$$\lambda_m = \frac{A}{T}, \tag{11b}$$

where A is a *constant*.

The constant A has the value 0.2883 cm. deg. Hence, for $\lambda_m = 0.55\ \mu$ (the wave-length for which the human eye is most sensitive), $T = 5240°$ K. approximately. This would, therefore, be the temperature at which a black-body radiator would emit light of the same distribution as is actually emitted by the sun at a somewhat higher temperature (about 6000° K.).

By making use of equation (3), equation (10) may evidently be expressed in the form

$$K_\lambda = \frac{c^2}{\lambda^5} F\left(\frac{c}{\lambda T}\right). \tag{12}$$

[1] *Wied. Ann.*, **52**, 132 (1894). M. Planck, Theory of Radiation, Eng. Trans. by Massius.

Combining this relation with equation (11*b*) and differentiating, it follows that

$$K_{\lambda_m} = B.T^5. \tag{13}$$

That is, the maximum intensity of a black-body radiator varies as the fifth power of the absolute temperature.

The next problem that presented itself was the determination of the function F. In order to accomplish this, Wien introduced two additional assumptions of a questionable nature regarding the mechanism of radiation and deduced the relation

$$K_\nu = \frac{\alpha\nu^3}{c^2}\epsilon^{-(\beta\nu/T)}, \tag{14}$$

where α and β are constants. Expressed in terms of wave-lengths, this relation becomes

$$K_\lambda = \left(\frac{c_1}{\lambda^5}\right)\cdot\epsilon^{-(c_2/\lambda T)}. \tag{15}$$

This form of Wien's Radiation Law is the one most generally used and c_1 and c_2 are referred to as the constants in Wien's equation.[1]

A comparison of this equation with the measurements of Lummer and Pringsheim showed, however, that there is agreement only for low values of λT. Thus Wien's equation is perfectly satisfactory for frequencies in the visible and ultra-violet regions, even at the highest temperature, but fails completely when applied to heat waves and radiations of longer wave-length.

On the other hand, Lord Rayleigh and Jeans, basing their arguments on the classical theory, derived a distribution law which has been found to be in agreement with the observations for high values of λT (that is, longer wave-lengths) but breaks down completely when applied to the spectral region in which Wien's equation is valid. Since the Rayleigh-Jeans equation involves no additional assumptions except that of the validity of Newtonian dynamics when applied to radiation, it is necessary to discuss the fundamental principle on which this equation was based. This is all the more essential because the quantum theory represents a complete severance from this apparently well-founded principle which is known as that of the equipartition of energy.

Principle of Equipartition of Energy: According to the kinetic theory of gases, the average kinetic energy K of the molecules of a gas at any temperature T is given as

$$K = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT,$$

where N = number of molecules per mole = 6.061×10^{23}, k = Boltzmann's gas constant= 1.372×10^{-16} erg/deg., and $R = 8.315 \times 10^7$ erg/deg. per mole, = 1.987 cal./deg per mole.

[1] A complete discussion of Wien's equation and a comparison with the data of Lummer and Pringsheim are given by W. Wien and O. Lummer in *Rapports du Congres International de Physique*, **2**, 23–99 (1900).

The direction of the motion corresponding to this translational energy can be represented by three space-coördinates, and if $\frac{dx}{dt}$, $\frac{dy}{dt}$, and $\frac{dz}{dt}$ represents the velocity-components along three rectangular coördinates, the average kinetic energy of motion is given by the relation

$$\tfrac{3}{2}kT = \tfrac{1}{2}mv^2 = \tfrac{1}{2}m\left\{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right\},$$

where v is the velocity along the direction of motion, and m is the mass of the molecule. It is evident that, in a mass of gas, the average kinetic energy along each of the three coördinates must be the same. Thus, we arrive at the conclusion that the average kinetic energy of a molecule is $\frac{1}{2}kT$ for each of the three directions in which it can move.

Now let us consider the bearing of this conclusion on the problem of specific heat of gases. If in the case of a monatomic gas we assume that the only effect of an increase in the temperature of a mass of the gas maintained at constant volume is to increase the kinetic energy of agitation of the molecules, then the heat capacity per mol. at constant volume (C_v) ought to be $\frac{3}{2}Nk = \frac{3}{2}R$, that is, 2.98 calories. Furthermore, in the case of any "perfect" gas, the energy absorbed per mol. in expanding at constant pressure is R calories per degree. Consequently the specific heat at constant pressure (C_p) for a monatomic gas ought to be $\frac{5}{2}R$. These deductions have actually been found to be valid and the conclusion is therefore drawn that any rotational energy which the molecules of a monatomic gas may possess is of no importance in regard to the heat capacity.

In the case of diatomic gases, Boltzmann considered the molecule as having a dumbbell sort of structure, with fixed distance between the atoms. On collisions with other molecules it is assumed that the atoms are set in rotation about an axis passing through the center of the line joining them. To describe this rotation requires two coördinates, viz., the inclination of the axis of the dumbbell to that of rotation and the angular velocity about the axis of rotation. Hence, a diatomic molecule should possess altogether five degrees of freedom, three to describe the translational motion of the molecule as a whole and two to correspond to the rotation of the atoms.

If the average kinetic energy of a molecule is $\frac{1}{2}kT$ for each degree of movability, more generally known as *degree of freedom*, the heat capacity per gram-molecule of a diatomic gas ought to be $\frac{5}{2}R$. This deduction was again found to be in agreement with experimental data.

But not only was Boltzmann able in this manner to calculate the specific heats of gases, he also applied the same considerations to solids and thus arrived at an explanation of the Dulong and Petit law. According to this law the product of specific heat and atomic weight in the case of elements in the solid state is a constant which has a value of about 6 calories. This law was derived empirically at the beginning of the nineteenth century; but until

Now for a number of years a gradually increasing number of facts had led many physicists to question the general validity of the principle of equipartition of energy. For one thing, while the law of Dulong and Petit is pretty generally true, the number of exceptions to it had been accumulating during the past century. Thus, it was known that carbon, boron, and silicon have atomic heats lower than 6; but it was also observed that the atomic heats of these elements increase with temperature, and at high enough temperatures they behave "normally." Furthermore, the molecular heats of some diatomic gases like chlorine and bromine are nearly a calorie too high even at ordinary temperatures, and they become even greater at higher temperatures.

To explain these facts it would be necessary to assume that the number of degrees of freedom of a carbon atom or chlorine molecule increases gradually with the temperature. But, the Boltzmann concept leaves no room for such a transition stage. An atom or molecule must possess a certain integral number of degrees of freedom; a degree of movability in any definite manner is either absent or present. There can be no *gradual acquisition* by any body of a degree of freedom. The conception of integral degrees of freedom thus presents many difficulties. Furthermore, it has been shown above that, in the realm of radiant phenomena, similar difficulties are present. The principle of equipartition of energy cannot, therefore, be of as general validity as hitherto assumed. But this principle was deduced from the fundamental laws of dynamics, and is, therefore, just as valid as the latter. Here then was a Gordian knot that appeared as difficult to untie as the one of classical fame. It remained for Planck to apply to this case a similar remedy.

Planck starts out with a denial of the general validity of the principle of equipartition but makes use of the fundamental electro-dynamical equations in deducing his radiation formula. Doubt may be cast upon the theory, therefore, because of its assumptions; but that the conclusions from his assumptions are in excellent accord with experiment is undeniable. Furthermore, the fact that his arguments have been successfully extended into regions undreamt of when the theory was enunciated gives the latter the most prominent place in contemporary physics.

Planck's theory of black-body radiation contains three groups of assumptions: Firstly, he assumes that there exists in the enclosure linear oscillators similar to those used in the production of Hertzian waves but of molecular dimensions, so that the frequencies of the harmonic vibrations emitted by them are of the order of magnitude of those present in the radiation from a black body. As in the previous section, the relation between K_ν, the intensity of the radiation of frequency ν and the mean energy of the oscillator U_ν is given by equation (16),

$$U_\nu = \frac{c^2}{\nu^2} K_\nu. \tag{16}$$

If there are present in the enclosure N oscillators of frequency ν, each having a mean energy U_ν, the total energy is NU_ν.

Now, as we have seen above, the principle of equi-partition of energy would demand for each oscillator an average energy of kT (cf. equation (17)), and the combination of this with equation (16) leads to the Rayleigh equation. This equation would ascribe to each oscillator an average energy greater than that found experimentally. The fact, however, that the Rayleigh equation holds for large values of T shows that the average energy approximates more and more to kT as the temperature is increased.

This circumstance leads Planck to make the second of his assumptions: that an oscillator cannot take up energy continuously, *but discontinuously in multiples of a unit quantum* δ. As the temperature increases, the value of this multiple, $n\delta$, approximates more and more nearly to kT. The problem therefore to be solved is this: What is the average energy of an oscillator when it can take up or give out only a definite fraction, $\frac{\delta}{kT}$, of this at any instant? The theory of probability leads to the relation

$$U_\nu = \frac{\delta}{\epsilon^{\delta/kT} - 1} \cdot \tag{21}$$

Combining this with equation (16),

$$K_\nu = \frac{\nu^2}{c^2} \frac{\delta}{\epsilon^{\delta/kT} - 1} \cdot \tag{22}$$

For $\delta = 0$ this equation becomes the same as the Rayleigh equation, as we would expect, since the theory of Planck differs from that of Rayleigh in the fact that the former assumes a discontinuous variation of energy in an oscillator, while Rayleigh assumes the variation to be continuous.

The similarity of equation (22) with Wien's formula leads to the third and last assumption made by Planck. He assumes that the unit quantum which the oscillator can emit or absorb is proportional to its frequency, ν; that is,

$$\delta = h\nu, \tag{23}$$

where h is a universal constant.

Substituting $h\nu$ for δ in equation (22) leads to the Planck equation which may be written in the form

$$E_\nu = \frac{2\pi\nu^2}{c^2} \cdot \frac{h\nu}{\epsilon^{h\nu/kT} - 1} \tag{24}$$

or

$$E_\lambda = \frac{2\pi c^2 h \lambda^{-5}}{\epsilon^{ch/k\lambda T} - 1} \tag{25}$$

and

$$u_\nu = \frac{4}{c} E_\nu = \frac{8\pi h\nu^3}{c^3 \cdot (\epsilon^{h\nu/kT} - 1)} \cdot \tag{26}$$

The obvious weakness in this argument is the fact that while Planck denies the validity of the principles of equi-partitions of energy and, consequently, of the fundamental dynamical equations upon which this principle is based, he yet assumes the validity of the electro-dynamical equations, which are also deduced from these fundamental equations.

In deriving the radiation formulæ of Rayleigh and Planck it has been assumed so far that the radiation is due to linear oscillators each vibrating with a definite frequency ν and emitting or absorbing radiation of the corresponding frequency. As this assumption may appear to be quite arbitrary, it is of interest to show that the same results are obtained if we confine our attention to the radiation alone and apply to this the principle of equi-partition.[1]

For this purpose it is necessary to assign to the radiation itself degrees of freedom. Such a concept is certainly not very easy to grasp physically, but from ordinary electro-dynamical considerations it may be shown that the number of degrees of freedom corresponding to radiation between the frequencies ν and $\nu + d\nu$ is $\frac{8\pi}{c^3} \cdot \nu^2 d\nu$ per unit volume. Applying the principle of equi-partition, we must ascribe to each degree of freedom a kinetic energy $\frac{1}{2}kT$ and since the average kinetic energy is equal to the average potential energy, the total energy density per unit volume must be

$$u_\nu d\nu = \frac{8\pi}{c^3} kT\nu^2 d\nu \text{ ergs per cm.}^3.$$

From equation (5) it follows that

$$K_\nu = \frac{\nu^2}{c^2} kT. \tag{18}$$

That is, we obtain the Rayleigh-Jeans equation, and as has been shown already, this leads to the conclusion that the total radiant energy per unit volume in equilibrium with matter should be infinite, whereas actually we know it to be finite.

It is this phenomenon that leads to the discarding of Newtonian mechanics as applied to radiation.

"Assuming for the moment," Jeans states,[2] "the truth of this as an experimental fact, we may try to illustrate its physical bearings. To make the question as definite and as simple as possible, let us fix our attention on an enclosure with perfectly reflecting walls in which there is a mass of, say, iron at 0° C., and let us suppose that there is a state of equilibrium inside this enclosure. The iron is continually radiating energy out from its surface into the surrounding ether inside the enclosure, and is also absorbing energy from the ether. From the condition of equilibrium, the rates of exchange must just balance. If we assume, for additional simplicity, that the iron is coated with a perfectly absorbing paint, then in point of fact each square centimeter of surface emits 3×10^5 ergs of radiation per second

[1] The derivation of Planck's equation from this point of view is given in a very simple form by J. Rice, An Elementary Account of the Quantum Theory, *Trans. Farad. Soc.*, 11, Part 1, p. 1 (1915).

[2] Report on Radiation and the Quantum Theory; London, 1914.

into the ether; and also absorbs 3×10^5 ergs per second of radiation falling on to it from the ether. The energy in the ether is of density 4×10^{-5} ergs per cubic centimeter; the heat energy in the iron is of the order of 8×10^9 ergs per cubic centimeter. The heat energy of the iron resides in the oscillations of its atoms, each atom moving with an average velocity of about 30,000 cms. per second.

"A very little consideration will show that this state of things is different from what might be expected by analogy from other systems which are known to obey the ordinary dynamical laws. Consider, for instance, a tank of water (to represent the ether) in which is floated a system of corks (to represent atoms of matter) connected by light springs or elastics so that they can oscillate relatively to one another. Suppose that initially the surface of the water is at rest. Let the system of corks be set into violent oscillation and placed on the surface of the water. The motion of the corks will set up waves in the water, and these waves will spread all over the surface of the water, undergoing reflection when they meet the walls of the tank. We know that ultimately the corks will be reduced to rest; the energy of their motion will be transformed first into the energy of waves and ripples on the surface of the water, and then, owing to the viscosity of the water, into heat energy in the water. A final state in which the corks continue to oscillate with extreme vigor while the water has almost no energy is unthinkable; we expect a final state in which practically all the energy has found its way into the water."

In a similar manner we find that "in all known media there is a tendency for the energy of any systems moving in the medium to be transferred to the medium and ultimately to be found, when a steady state has been reached, in the shortest vibrations of which the medium is capable. This tendency can be shown to be a direct consequence of the Newtonian laws. This tendency is not observed in the crucial phenomenon of radiation; the inference is that the radiation phenomenon is determined by laws other than the Newtonian laws."

Einstein's Derivation of Planck's Radiation Law: Objection has been made to Planck's arguments, since he uses the results of the electro-magnetic theory in deriving a relation between radiation density for any frequency and the energy of the corresponding oscillator while he completely discards the principle of equi-partition when dealing with the distribution of energy among the oscillators. It is, therefore, of interest to point out the manner in which Einstein has arrived at the same result as Planck by means of totally different considerations.[1]

In order to understand Einstein's discussion, it is necessary to refer briefly to what is known as Boltzmann's principle. Suppose we have an atomic or molecular system of which the individual atoms or molecules are capable of existing in a number of different states, Z_1, Z_2, $\cdots$ Z_m $\cdots$ Z_n. Let E_1, E_2, $\cdots$ E_m $\cdots$ E_n denote the corresponding energies of the molecules in these states. By this quantity, E, must be understood the potential energy of the molecule in any one state. When a molecule passes from any state Z_m to any other state Z_n, the energy difference involved is given by $E_n - E_m$. According to Boltzmann's principle, if N denote the total number of molecules, the number of molecules N_m, which are present at any instant in state Z_m at temperature T, is given by the relation

$$\frac{N_m}{N} = p_m \epsilon^{-(E_m/kT)}, \tag{27}$$

where k = Boltzmann's gas constant, and p_m denotes a constant which is characteristic of the state Z_m and independent of T.

[1] *Ber. deut. phys. Ges.*, **18**, 318 (1916); also *Phys. Z.*, **18**, 121 (1917).

It has appeared to the writer that this relation may be derived in a relatively simple manner by combining the deductions of the kinetic theory with those of the second law of thermodynamics.

Let us consider a reaction of the type

$$Z_1 \rightleftarrows Z_2.$$

The velocity of the reaction $Z_1 \rightarrow Z_2$ is given by

$$v_1 = k'[Z_1],$$

where $[Z_1]$ = concentration of molecules Z_1. Similarly, the velocity of the reaction $Z_2 \rightarrow Z_1$ is given by

$$v_2 = k''[Z_2].$$

The constants k' and k'' have the dimensions of a frequency and denote the fraction of Z_1 or Z_2 which is undergoing a transition per unit time.

At equilibrium, the velocities of the opposing reactions are equal and hence

$$\frac{[Z_2]}{[Z_1]} = \frac{k'}{k''} = K,$$

where K denotes the equilibrium constant of the reaction.

According to the second law of thermodynamics, we have the relation

$$\frac{d\ln K}{dT} = \frac{\Delta E}{kT^2},$$

where ΔE is the total energy change in the reaction *per molecule* of Z_1 or Z_2.

Assuming ΔE to be independent of the temperature, the last relation may also be expressed in the form

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta E}{k}.$$

Integrating this equation, we obtain the relation

$$K = K_0 \epsilon^{-(\Delta E/kT)},$$

where K_0 is an integration constant.

Hence,

$$\frac{k'}{k''} = K_0 \epsilon^{-(\Delta E/kT)}.$$

If we denote the energy of the molecule in state Z_1 by E_1 and in state Z_2 by E_2, we can evidently write

$$\frac{k'}{k''} = K_0 \frac{\epsilon^{-(E_2/kT)}}{\epsilon^{-(E_1/kT)}} = \frac{[Z_2]}{[Z_1]}.$$

Consequently

$$[Z_2] = p_2 \epsilon^{-(E_2/kT)}$$

and

$$[Z_1] = p_1\epsilon^{-(E_1/kT)},$$

where $p_2/p_1 = K_0$.

We may now return to the discussion of Einstein's derivation of Planck's relation.

Let us consider a gas whose molecules are in equilibrium with radiation at a certain temperature. According to classical theory, the energy per molecule can vary continuously from zero to infinity in accordance with the Maxwell-Boltzmann distribution law. However, we must postulate as the fundamental assumption of the quantum theory that such a continuous variation in energy content is impossible. *Each molecule is capable of existing only in a series of discrete states* Z_1, Z_2, $\cdots$ Z_m $\cdots$ Z_n, *for which the corresponding energies are* E_1, E_2, *etc.*

Every energy change in such a system including the emission or absorption of radiant energy occurs because of the transition of molecules from one of these states to some other. Bohr, to whom we owe the introduction of this postulate into the quantum theory, has designated Z_1, Z_2, $\cdots$ Z_m, $\cdots$ Z_n as "stationary" states of the system.

The relative number of the molecules which are present at any instant in any given state Z_n will evidently be given by Boltzmann's equation (27).

We shall assume that the energy $E_m - E_n$ is emitted when the molecule passes from state Z_m to state Z_n. Hence the same amount of energy is absorbed when the reverse reaction occurs. A molecule can pass from state Z_m to Z_n in two ways. Firstly, there may be a spontaneous transition, such as is undergone by radioactive elements.

The rate at which this reaction occurs is given by

$$-\frac{dN_m}{dt} = A_m{}^n N_m, \tag{28}$$

where $A_m{}^n$ is a constant characteristic of this reaction. It is evident that $1/A_m{}^n$ corresponds to the so-called average life of the atom Z_m under these conditions where only spontaneous transitions can occur.

Since, however, the molecule is present in an environment which is filled with radiation corresponding to the temperature T, the reaction $Z_m \rightleftarrows Z_n$ is also influenced by this radiation. Let u_ν denote the density of the radiation corresponding to frequency ν. We assume that the reaction $Z_m \rightarrow Z_n$ occurs with simultaneous *emission of monochromatic radiation of frequency* ν, and that the reverse reaction occurs with absorption of radiation of the same frequency. The rate of the reaction in either direction depends upon the value of u_ν. Consequently

$$\left.\begin{aligned} -\frac{dN_m}{dt} &= B_m{}^n N_m u_\nu \\ \text{and} \qquad -\frac{dN_n}{dt} &= B_n{}^m N_n u_\nu. \end{aligned}\right\} \tag{29}$$

Again, the constants $B_m{}^n$ and $B_n{}^m$ are of the same nature as the constant $A_m{}^n$.

It is important to realize fully the significance of the assumption involved in equations (29). It is assumed that the molecule Z_m or Z_n may be stimulated by radiation of frequency ν *which is characteristic of the reaction* $Z_m \rightleftarrows Z_n$, and while it is relatively easy to understand how the reaction $Z_n \rightarrow Z_m$ can occur by absorption of energy from the environment, it is not so obvious that the reverse reaction may occur with emission of energy to the environment. Such an assumption is at variance with our classical conception of the law of conservation of energy. However, the opinion has been growing among a large number of physicists that the law of conservation of energy is only true statistically, that is, for a large number of molecules.[1]

Furthermore, we shall find that this assumption is absolutely essential in order to account for photo-electric phenomena, photo-chemical reactions and possibly unimolecular thermal reactions.

Now, at equilibrium, the velocities of the two reactions $Z_m \rightleftarrows Z_n$ are equal. Consequently

$$A_m{}^n N_m + B_m{}^n N_m u_\nu = B_n{}^m N_n u_\nu. \tag{30}$$

Substituting from equation (27), it follows that

$$(A_m{}^n + B_m{}^n u_\nu) p_m \epsilon^{-(E_m/kT)} = B_n{}^m p_n u_\nu \epsilon^{-(E_n/kT)},$$

that is,

$$A_m{}^n p_m = u_\nu (B_n{}^m p_n \epsilon^{(E_m - E_n)/kT} - B_m{}^n p_m). \tag{31}$$

At infinitely high temperatures the exponential factor obviously tends towards unity. Also u_ν increases to infinitely large values at the same time. Since, however, $A_m{}^n p_m$ is a finite quantity independent of T, it follows that

$$B_n{}^m p_n = B_m{}^n p_m \tag{32}$$

and, if we denote the ratio $A_m{}^n / B_m{}^n$ by α_{mn}, we can replace (31) by the equation

$$u_\nu = \frac{\alpha_{mn}}{\epsilon^{[(E_m - E_n)/kT]} - 1}. \tag{33}$$

In order to derive Planck's law from equation (33), it is necessary to compare the latter with the deductions arrived at by Wien and also by Rayleigh and Jeans.

As shown by Wien, it follows from the application of the second law of thermodynamics that

$$u_\nu = \frac{8\pi\nu^3}{c^3} F\left(\frac{\nu}{T}\right).^2 \tag{34}$$

Hence

$$\alpha_{mn} = \alpha\nu^3 \tag{35}$$

[1] See, for example, D. L. Webster, The Present Conception of Atomic Structure, *Nat. Res. Bull.*, Vol. 2, Part 6, p. 354 (1921).

[2] See equations (5) and (10) of preceding sections.

and

$$E_m - E_n = h\nu, \tag{36}$$

where h and α are constants.

On the other hand, we know that the equi-partition law and the Rayleigh-Jeans relation deduced on the basis of this law are valid at very large values of T.

Under these conditions,

$$u_\nu = \frac{8\pi\nu^2}{c^3} kT \tag{37}$$

But, from equation (33), it is also evident that for extremely high values of T, $\frac{E_m - E_n}{kT}$ is a very small fraction and consequently the equation may be written in the form

$$u_\nu = \frac{\alpha\nu^3 \cdot kT}{(E_m - E_n)}$$

$$= \frac{\alpha\nu^3 \cdot kT}{h\nu} \cdot \tag{38}$$

Comparing (38) with (37), we obtain the relation

$$\alpha = \frac{8\pi h}{c^3}$$

and hence the final expression for the radiation law may be written in the form

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{\epsilon^{h\nu/kT} - 1} \cdot \tag{26}$$

Equation (36) which has been derived above by introducing Wien's displacement law was first postulated by N. Bohr in connection with his theory of atomic structure in the following form: If we assume an atomic system such as that discussed already, in which the molecules or atoms can exist only in a series of "stationary" states, then the radiant energy emitted or absorbed in any transition is *monochromatic* and the frequency ν is determined by the condition

$$E_m - E_n = h\nu,$$

that is, equation (36).

These two postulates, viz., that of the existence of stationary states and that governing the transitions between the different states, form the most important guiding principles for the application of the quantum theory to chemical and physical phenomena.

Radiation Constants: The very large number of investigations carried out in recent years on the determination of the value of h has been summarized by

R. T. Birge [1] and R. Ladenburg.[2] The former arrives at the value $h = (6.5543 \pm 0.0025) \times 10^{-27}$ erg sec., while Ladenburg concludes that the most probable value is 6.54×10^{-27}. Using the value $h = 6.554 \times 10^{-27}$, it is possible to derive the values of the radiation constants involved in the equations given in the preceding sections.[3]

The factor $2\pi c^2 h$ in equation (25) is usually designated as C or often as C_1,[4] while ch/k is denoted by C_2.

Substituting in these factors the values

$$c = 2.9986 \times 10^{10} \text{ cm. sec.}^{-1}$$

and

$$k = 1.372 \times 10^{-16} \text{ erg deg.}^{-1},$$

we obtain the values

$$C_1 = 2\pi c^2 h = 3.703 \times 10^{-5} \text{ erg cm.}^{-2} \text{ deg.}^{-1},$$
$$C_2 = ch/k = 1.433 \text{ cm. deg.}$$

If we differentiate equation (25) with respect to λ and equate the result to zero, we obtain the value of the wave-length λ_m, at which E_λ is a maximum. The resulting equation may readily be reduced to the following form:

$$\epsilon^{-(ch/k\lambda_m T)} - 1 + \frac{ch}{5k\lambda_m T} = 0.$$

This equation may be solved graphically and leads to the result

$$\frac{ch}{k\lambda_m T} = 4.9651,$$

that is,

$$\lambda_m T = \frac{ch}{4.9651k} = 0.2885 \text{ cm. deg.}$$

The value of E_λ corresponding to λ_m is given by the relation

$$E_{\lambda_m} = \frac{2\pi k^5 (4.9651)^5 T^5}{c^3 h^4 (\epsilon^{4.9651} - 1)}$$
$$= 1.301 \times 10^{-4} T^5 \text{ erg cm.}^{-3} \text{ sec.}^{-1}.$$

To calculate the constant σ in the Stefan-Boltzmann relation, it is necessary to perform the integration corresponding to the relation

$$E = \int_0^\infty E_\lambda d\lambda = \sigma(T^4 - T_0^4).$$

[1] *Phys. Rev.*, **14**, 361 (1919).

[2] *Jahrbuch d. Elektronik*, **17**, 93 (1910).

[3] The values given here are those adopted in the International Critical Tables.

[4] Unfortunately many writers, when referring to Planck's and Wien's equations, use the expression for K_ν and K_λ; others use the relations for E_ν and E_λ. Consequently the values of C_1 differ by the factor 2π according as one or the other form is used.

The integration leads to the following value for σ:[1]

$$\sigma = \frac{12\pi \times 1.0823k^4}{c^2h^3}$$

$$= 5.709 \times 10^{-5} \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-4}.$$

This value of σ is in good agreement with the most recent experimental determinations.[2]

Finally, corresponding to equation (8) for u, the total radiation density, we have according to equation (9)

$$\alpha = \frac{4}{c}\sigma = 7.616 \times 10^{-15} \text{ erg. cm}^{-3}. \text{ deg}^{-4}.$$

Quantum Theory and Velocity of Chemical Reactions

The Einstein Photo-chemical Equivalent Law: As mentioned in connection with Einstein's derivation of Planck's radiation law, the relation

$$\Delta E = Nh\nu \tag{1}$$

is of fundamental importance in all of the applications of the quantum theory. In this equation ΔE denotes the difference in energy (per gram-molecular weight) between two different states of a system and ν is the frequency of monochromatic radiation absorbed or emitted during the transition from one state to the other.

The application of equation (1) to the photo-electric effect and the inverse phenomenon has been discussed in a previous section. In these cases, the energy ΔE referred to the change in kinetic energy of an electron when emitted or absorbed by an atomic system. In other words, in all the applications of equation (1) considered in the preceding, it has been a question of the interaction between radiation and electrons.

Since, according to our present views, all chemical reactions involve some changes in the configurations of the electrons in the reacting atoms, it would be expected that, at least under certain conditions, equation (1) might be applied to even purely chemical reactions.

A step in this direction was taken by Einstein when he suggested his photo-chemical equivalent law.[3] According to this law, the amount of energy absorbed per gram-molecular weight of a photo-sensitive substance is $Nh\nu_0$, where ν_0 corresponds to the frequency of the luminous or ultra-violet radiation which

[1] For complete details regarding the mathematical methods used in carrying out this integration and also the differentiation in connection with the evaluation of $\lambda_m T$, the reader may consult the comprehensive treatise by K. Jellinek, entitled Physikalische Chemie der Gasreaktionen (Leipzig, 1913), pp. 351–356.

[2] W. W. Coblentz, Scientific Papers, Bu. Stand. No. 405 (1921). This contains a complete bibliography of the previous investigations.

[3] *Ann. Physik*, **37**, 832 (1912).

is absorbed by the reacting substance. Bodenstein and Dux[1] showed that this law is approximately valid for a number of reactions which they designate as primary reactions. In other cases, the primary photo-chemical reaction is probably masked by secondary phenomena so that no experimental test can be obtained of the validity of Einstein's law.

In deriving his law, Einstein assumed that the velocity of a photo-chemical reaction is proportional to the density of the radiation of frequency ν_0 present in the system. M. Perrin and W. C. McC. Lewis have attempted to extend this idea to cover purely thermal as well as photo-chemical reactions. Although this suggestion has been found to be untenable, nevertheless it merits consideration because it has led to a great deal of interesting discussion regarding the actual mechanism by which molecules are made capable of entering into chemical reaction.

Velocity of Chemical Reactions and Statistical Mechanics: Before discussing this theory, which is known as the radiation hypothesis of chemical reactions, it is necessary to point out that, as shown in a previous section, it is possible, on the basis of van't Hoff's equation, to derive an expression for the velocity of a chemical reaction as a function of the temperature. If k_1 and k_2 denote the velocity constants of the two opposing reactions leading to equilibrium, then

$$\left.\begin{aligned} \frac{d\ln k_2}{dT} &= \frac{E_2}{RT^2} \\ \text{and} \qquad \frac{d\ln k_1}{dT} &= \frac{E_1}{RT^2} \end{aligned}\right\} \tag{2}$$

where $E_2 - E_1 = Q$, the heat of reaction, and $k_2/k_1 = K$, the equilibrium constant. For the purpose of calculation by ordinary logarithms, these relations may be expressed in the more convenient form

$$\frac{d\log k}{d\left(\frac{1}{T}\right)} = -\frac{E}{4.571}. \tag{3}$$

Thus if $E = 10{,}000$ calories (a rather low value, as will be seen from the subsequent considerations), it follows from equation (3) that k_1 or k_2 will increase about 71 per cent when the temperature increases from $T = 300$ to $T = 310$.

In general, as has been known for a long time, the velocity constant of a thermal reaction doubles or trebles with a rise of temperature of 10° C., thus corresponding to rather large values of E.[2] It is the existence of this extraordinary temperature-coefficient of reaction velocity that has proven extremely

[1] *Z. physik. Chem.*, **85**, 297 (1913).

[2] For illustrations the reader is referred to the classical discussion of this topic in van't Hoff's Die Chemische Dynamik, 2d Ed. (1901), pp. 226–231, and to Chapter XIV.

difficult to understand. S. Arrhenius [1] suggested that in any system of molecules at a given temperature only a certain fraction of the molecules are "active," that is, capable of reacting, and as the temperature rises, the fraction of molecules in the active state increases. Furthermore, Arrhenius showed that equation (2) must necessarily express the relation between velocity constant and temperature.

By applying the considerations of statistical mechanics, Marcelin [2] and Rice [3] arrived at a relation which is the same as that expressed by equations (2) above. They assume that E corresponds to the energy necessary to convert 1 mole of normal molecules into the active state. According to Boltzmann's distribution law, the fraction, f, of the molecules which will be in the activated state (that is, possess an energy content which exceeds that of normal molecules by E cal. per mole) at temperature T is given by

$$f = \epsilon^{-(E/RT)}.$$

Hence

$$\frac{dlnf}{dT} = \frac{E}{RT^2} \tag{4}$$

and since the velocity is proportional to f, equation (2) follows as a necessary consequence.

According to this theory, therefore, E_2 and E_1 in equations (2) denote the heats of activation for the molecules taking part in the corresponding reactions, and the total energy change (which is the thermally measured heat of reaction) is the difference between the activating or "critical" energies.

Radiation Theory of Chemical Reactions: [4] It is obvious that the discussion in the previous section offers no explanation as to the actual mechanism by which molecules become activated. As is often the case in any scientific speculation regarding an unexplained phenomenon, we think we have arrived at an understanding of it when we have labelled it by another name.

However, M. Trautz [5] and subsequently J. Perrin [6] and W. C. McC. Lewis [7] have advanced the hypothesis that "possibly the infra-red radiation which is necessarily present throughout any system in virtue of its temperature may be the active agency in promoting chemical change of the ordinary or thermal type, such changes including not only the so-called uncatalyzed reactions, but catalyzed reactions as well, in so far at least as these are met with in homogeneous systems.

[1] *Z. physik. Chem.*, **4**, 226 (1889).

[2] *Compt. rend.*, **157**, 1419 (1913); **158**, 116, 407 (1914). *Ann. Physique*, (9) **3**, 120 (1915).

[3] *Brit. Ass. Rep.*, **1915**, p. 397.

[4] An excellent discussion of this theory has recently been published by H. S. Harned, *J. Franklin Inst.*, **196**, 181 (1923).

[5] A summary of his work with references to earlier papers is given by Trautz in *Z. anorg. Chem.*, **102**, 81–129 (1918), and **106**, 149 (1919).

[6] *Ann. Physique*, (9) **11**, 5–108 (1919).

[7] *J. Chem. Soc.*, **109**, 796 (1916); **111**, 389, 457, 1086 (1917). *Phil. Mag.*, **39**, 26 (1920); also Quantum Theory, pp. 138–143 (1919 Edition).

"Briefly the hypothesis is, that the increase in internal energy which a molecule must receive before it is capable of reacting (that is, the critical increment E) is communicated to it by infra-red radiant energy present in the system, the addition of energy being made in terms of quanta of the absorbable type." [1]

Perrin has stated the hypothesis in the following form: "All chemical reaction is provoked by radiation; its velocity is determined by the intensity of that radiation and depends only on the temperature in the measure that the intensity depends upon it." [2]

Thus, the radiation-hypothesis represents an extension of Einstein's law of the photo-chemical equivalent to thermal reactions. In accordance, therefore, with this hypothesis, the chemical action depends upon the absorption of a nearly monochromatic radiation of frequency ν given by the relation

$$E_c = Nh\nu, \tag{5}$$

where E_c denotes the critical increment or energy necessary to activate 1 mole. Furthermore, it follows that the increase in velocity of the reaction with temperature must be due to the increase in radiation density $u_\nu d\nu$ of this radiation, and therefore the temperature-coefficient of the velocity constant should be the same as that of the energy density $u_\nu d\nu$.

The range $d\nu$ would correspond, according to this point of view, to a narrow region of the spectrum which is absorbed by the molecules taking part in the reaction.

Substituting for $u_\nu d\nu$ the relation derived by Planck, it follows that the velocity constant of a reaction is given by a relation of the form

$$k = C \cdot \frac{8\pi\nu^2 \cdot h\nu}{\epsilon^{h\nu/kT} - 1} d\nu,$$

where C is a constant.

Replacing Planck's relation by Wien's (which may be done in this case without introducing any appreciable error), it is evident that the velocity constant may be expressed as a function of the temperature by the relation

$$\left.\begin{aligned} k &= k_0\epsilon^{-h\nu/kT} = k_0\epsilon^{-Nh\nu/RT} \\ \text{and} \\ \frac{d\ln k}{dT} &= \frac{Nh\nu}{RT^2} \end{aligned}\right\} \tag{6}$$

where k_0 corresponds to the limiting value of the velocity constant at infinitely higher temperatures.

[1] W. C. McC. Lewis, *J. Chem. Soc.*, **109**, 796 (1916).

[2] Quoted by H. S. Harned, *loc. cit.*, p. 184.

Also if ν_1 corresponds to the activating frequency for the reaction in one direction and ν_2 to the activating frequency for the reverse reaction, then

$$\left.\begin{aligned} Q = E_2 - E_1 &= Nh(\nu_2 - \nu_1) \\ \text{and} \\ \frac{d\ln K}{dT} &= \frac{Nh(\nu_2 - \nu_1)}{RT^2} \end{aligned}\right\} \quad (7)$$

where Q and K have the significations mentioned previously.

In accordance with this theory it would be expected that the frequency ν calculated from the temperature-coefficient of the velocity constant should be the same as that absorbed by the reacting molecules, or at least there should be an absorption band which includes the radiation of frequency ν.

For the purpose of calculating this frequency, it is convenient to write equation (5) in the form

$$\begin{aligned} \nu = \frac{E_c}{Nh} &= \frac{E_c \times 4.184 \times 10^7}{6.062 \times 10^{23} \times 6.55 \times 10^{-27}} \\ &= 1.048 \times 10^{10} E_c, \end{aligned} \quad (8)$$

where E_c is expressed in calories per gm.-mol. and may be calculated from the temperature-coefficient of the velocity constant by equation (3).

It is worth noting in this connection that equation (7) had been previously deduced by F. Haber[1] and applied by him to the formation of halide salts from their elements. But, as shown in the present section, it follows logically from Einstein's photo-chemical equivalent law if we assume that similar considerations are valid for thermal reactions.

As support for the radiation theory, both Perrin and Lewis have pointed out that, for a number of reactions, the frequency ν calculated from E_c corresponds to a wave-length in an observed absorption band. On the other hand, there are also a large number of cases for which this is not true. This point, however, is discussed more fully in a subsequent part of this chapter.

Velocity of Bimolecular Reactions: By taking account of the fact that only a definite fraction of each type of molecule in a reacting system is capable of reacting at any given temperature, Trautz and W. C. McC. Lewis have shown that the rate of a bimolecular reaction in gases may be calculated from the frequency of collision between active molecules.

Let us consider a bimolecular reaction of the type $A + B \rightleftharpoons AB$ in a gaseous phase.

Let Q_A and Q_B denote the heats of activation per mole of A and B respectively. If n_A and n_B denote the total number of molecules per unit volume of each of these gases respectively, then the number of active molecules of A per unit volume is

$$n_A \epsilon^{-Q_A/RT}$$

[1] *Ber. deutsch. physik. Ges.*, **13**, 1117 (1911); K. Jellinek, Physikalische Chemie der Gasreaktionen (1913), p. 440.

and a similar expression must be valid for the concentration of active molecules of B.

Now let us assume that a molecule AB results at *every collision between active molecules* of A and B. Then the velocity of formation of AB is given by the number of collisions, Z, *between active molecules* of A and B per unit time and unit volume. According to the kinetic theory [1] of gases,

$$Z = n_A \epsilon^{-Q_A/RT} \cdot n_B \epsilon^{-Q_B/RT} \cdot \sigma^2 \sqrt{8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}, \tag{9}$$

where M_A = molecular weight of A, with corresponding notation for M_B, and σ denotes the *average molecular diameter of A and B*.

Hence the velocity of formation of AB,

$$\frac{dn_{AB}}{dt} = Z.$$

Comparing this with the ordinary expression for the rate of a bimolecular reaction,

$$\frac{d[AB]}{dt} = k_2[A][B],$$

where square brackets denote concentrations in *gram-mols. per cm.*^{3}, it follows that

$$k_2 = N\sigma^2 \sqrt{8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \cdot \epsilon^{-(Q_A+Q_B)/RT}, \tag{10}$$

where $N = 6.062 \times 10^{23}$.

Also it is evident that the total heat of activation $Q_A + Q_B$ is given by the relation

$$\frac{d\ln(k_2/\sqrt{T})}{d(1/T)} = -\frac{(Q_A + Q_B)}{R}. \tag{11}$$

W. C. McC. Lewis, and subsequently S. Dushman,[2] have tested the validity of the above relations for a number of bimolecular reactions in gases and found very good agreement between the observed values of k_2 and those calculated by means of equation (10). As an illustration, we shall cite the case of the reaction

$$H_2 + I_2 \rightarrow 2HI,$$

which has been investigated by Bodenstein.[3]

The values k_2 actually observed at different temperatures are given in the table. Plotting the values of $\log (k_2/\sqrt{T})$ against $1/T$, it is found that the best straight line which can be drawn through all the points corresponds to a value

[1] J. H. Jeans, The Dynamical Theory of Gases, 1916, Chapter X.

[2] *J. Am. Chem. Soc.*, **43**, 397 (1921).

[3] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

of $Q_{H_2} + Q_{I_2}$, as calculated from equation (11), which is equal to 42,000 calories.

For σ the value 3.26×10^{-8} cm. was used.

Since every collision between *active* H_2 and I_2 molecules yields 2HI, it is necessary in this case to multiply k_2 as calculated by means of equation (10) by the factor 2.

Thus the equation for k_2 may be expressed for the reaction under consideration, as follows:

$$\log k_2 = -\frac{42{,}000}{4.57T} + 0.5 \log T + 13.62.$$

Table IV gives a comparison between observed and calculated values of $\log k_2$.

TABLE IV

RATE OF FORMATION OF HI

T	Log k_2 (obs.)	Log k_2 (calc.)
556	0.647–2	0.46–2
579	0.120–1	0.13–1
599	0.737–1	0.67–1
629	0.402	0.41
647	0.718	0.83
666	1.151	1.23
683	1.391	1.58
700	1 808	1.91
716	2.146	2.22
781	3.126	3.30

The velocity of the inverse reaction $2HI \rightarrow H_2 + I_2$ has also been measured by Bodenstein over the same range of temperatures, and a calculation of the velocity constants based on the collision-frequency hypothesis gives results which are in good accord with the observed values.

Similar calculations have been carried out for a number of other reactions by W. C. McC. Lewis and also S. Dushman [1] and in nearly all cases the agreement with observed values is found to be good enough to show that the theory is at least very plausible.[2]

Velocity of Unimolecular Reactions: It is evident that the success attained in connection with the theory of bimolecular reaction velocities is not to be regarded as a confirmation of the radiation hypothesis. For there are involved in the former theory only two assumptions. (1) that only a fraction of the molecules are in a so-called active state, that is, capable of reacting, and (2) that reaction occurs whenever two activated molecules collide. There is no

[1] *Loc. cit.*

[2] The argument, however, is not entirely free from objection. It assumes, for example, that the reactions are entirely bimolecular gas reactions. Unpublished researches by H. A. Taylor show that the decomposition of hydrogen iodide is markedly accelerated by glass powder. Bodenstein's measurements may therefore be in part "wall" reactions. Also, adjustment of the value for σ, which can only be assumed, materially affects the agreement between theory and experiment.—Editor.

need of postulating any mechanism by which the molecules become activated. We merely introduce an assumption that active molecules exist in equilibrium with normal ones and apply to this condition the Boltzmann distribution law.

The case of unimolecular reactions is, however, more difficult to understand. Let us consider, for example, a unimolecular reaction such as the decomposition of PH_3 according to the equation:

$$2PH_3 \rightarrow 2P + 3H_2.$$

The velocity of this reaction was studied by M. Trautz and Bandharkar [1] and it was shown by them that the reaction is apparently uncatalyzed by the walls. The rate of such a reaction is given by the equation

$$-\frac{d\chi}{dt} = k_1\chi, \tag{12}$$

where χ denotes the amount of substance present at any instant and k_1 is the velocity-constant.

This equation is quite similar to that which expresses the rate of disintegration of a radioactive element. Integrating equation (12), we obtain the familiar relation

$$\chi = \chi_0^{-k_1 t}, \tag{13}$$

where χ_0 denotes the amount present at $t = 0$.

Now the most interesting fact about a unimolecular reaction is that the rate is *independent of the dilution* and depends only on the temperature. The constant k_1 denotes the relative decrease in the total amount of the reacting substance per unit time, while the reciprocal of this constant, that is, $1/k_1$, may be interpreted, as in the case of radioactive atoms, as the "average life" of a molecule of the substance which is dissociating.

Hence in the case of a unimolecular reaction the life of a molecule must be independent of the dilution and this leads to the conclusion that the life cannot be influenced in any direct manner by collision with other molecules. The fraction of the total amount present which is decomposed at the end of one second is always the same as long as the temperature is maintained constant.

[It must, however, be observed in this connection that there is, as yet, no unequivocal experimental evidence for the existence of unimolecular reactions (cf. Chapter XIV). It is to be expected that if such exist they will be found among gas reactions. Reactions in solution vary in velocity to a considerable degree with variation in the solvent, which fact points to the intervention of the solvent in the reaction and, therefore, to the absence of unimolecular reactions. Of the gas reactions suspected of being unimolecular the most discussed have been (1) the decomposition of phosphine, which was asserted by Trautz and Bandharkar [2] to be unimolecular in the gas phase between certain temperature limits and (2) the dissociation of nitrogen pen-

[1] *Z. anorg. Chem.*, **106**, 45 (1919).

[2] loc. cit.

toxide. Recent work by Hinshelwood [1] has shown that the former is not a gas reaction but is a typical wall reaction occurring at the surface of the containing vessel. The dissociation of nitrogen pentoxide was thought, as the result of the investigations of Daniels and Johnston [2] to be unimolecular. It is now known that it is a catalyzed reaction, nitrogen tetroxide being the catalyst. Hinshelwood and Prichard [3] have shown that other possible unimolecular reactions are not really unimolecular. This fact should therefore be borne in mind in reading the material of the following pages. The various proposals for the representation of such reaction velocity measurements can only be adequately tested when true unimolecular reactions are found and their velocities are measured.] [4]

If unimolecular reactions exist, we must apparently assume either (1) that the molecules receive the energy necessary for dissociation through the mechanism of collisions, or (2) that the molecules are decomposed by some external agency such as the black-body radiation with which any material system at a given temperature is in equilibrium. The first hypothesis is not permissible for the reasons already given. The second hypothesis was postulated by both Perrin and Lewis because it seemed to be the only possible explanation of the source of energy in unimolecular reactions. On this basis, as mentioned in a previous section, they derived the relation given in equation (6) in which the frequency of the activating radiation is given by the Einstein relation $Q_A = Nh\nu$.

Lewis has attempted to go one step further and deduce k_1 in terms of the radiation density at temperature T.[5] "According to the radiation hypothesis, the velocity constant should be obtained by dividing the rate of absorption of radiation of frequency ν by the quantity $h\nu$, the latter being the amount of energy required to decompose one molecule." However, on this basis the expression for the velocity constant is found to lead to a value which is only about one ten-millionth of that actually observed in reactions hitherto assumed to be unimolecular but now doubtfully so.

Trautz has assumed that the dissociation of a molecule is due to collisions between the constituent parts within the molecule; but the resulting expression for the velocity constant leads to values which are about one thousand times too great.[6]

There is an empirical method of deriving an expression for k_1 which has been suggested by Herzfeld.[7] At equilibrium the velocities of the opposing reactions are equal. Let us consider the dissociation $H_2 \rightleftarrows 2H$. The velocity of dissociation may be assumed to be unimolecular with a velocity constant k_1, while that of recombination must be bimolecular. The velocity constant, k_2,

[1] *J. Chem. Soc.*, **125**, 130 (1924).
[2] *J. Am. Chem. Soc.*, **43**, 53 (1921).
[3] *J. Chem. Soc.*, **128**, 2725, 2730 (1923).
[4] Editor's insertion.
[5] *Phil. Mag.*, **39**, 26 (1920); also *ibid.*, **46**, 327 (1923).
[6] R. C. Tolman, *J. Am. Chem. Soc.*, **43**, 269 (1921). S. Dushman, *loc. cit.*
[7] *Ann. Physik*, **59**, 635 (1919).

of the latter may be calculated on the basis of the kinetic theory as described already. Herzfeld assumes that every atom of hydrogen is in the active state, so that the rate of formation of H_2 is given by the rate at which hydrogen atoms collide. On the other hand, the equilibrium constant $K = k_1/k_2$ may be obtained from thermo-dynamical considerations and the Sackur-Tetrode formula for the chemical constant. In this manner Herzfeld has deduced the relation

$$k_1 = \frac{RT}{Nh}(1 - \epsilon^{-Nh\nu_A/RT})\epsilon^{-Q/RT}, \tag{14}$$

where ν_A is the vibration frequency of the atoms as derived from the specific heat data and Q is the heat of dissociation.

But the values of ν_A thus calculated are found to vary from 4×10^{14} to 9×10^{14} and therefore correspond to ultra-violet frequencies, whereas the vibration-frequencies deduced from specific heat data by Bjerrum and others vary from 10^{13} to 10^{14}. Since $Nh\nu_A$ is ordinarily very large compared to RT, Herzfeld's expression may be reduced to the form

$$k_1 = \frac{RT}{Nh}\epsilon^{-Q/RT}. \tag{15}$$

Hence

$$k_1 = \frac{1.987T \times 4.184 \times 10^7}{6.062 \times 10^{23} \times 6.554 \times 10^{-27}}\epsilon^{-Q/RT}$$
$$= 2.093 \times 10^{10}T\epsilon^{-Q/RT}$$

or

$$\log k_1 = 10.3208 + \log T - \frac{Q}{4.571T}. \tag{16}$$

For the dissociation of PH_3 at $T = 948$, k_1 observed is 1.2×10^{-2}, while Q, as determined from the temperature-coefficient of the velocity constant, is found to be 72,750 cal.[1]

Substituting in equation (16), we obtain for k_1 the value 3.22×10^{-4}, that is, a much smaller value than that observed.

A rather simple expression for the velocity constant of a unimolecular reaction has been suggested by S. Dushman[2] and has been found to agree much better with observed values than any of the other relations.

The considerations from which this expression is derived are as follows:

The velocity constant of a unimolecular reaction is independent of the volume and has the dimension of t^{-1} or a frequency. Combining this fact with the suggestion that the velocity depends upon the fraction of the molecules in the activated state, we obtain the expression

$$k_1 = \nu\epsilon^{-Q_A/RT}, \tag{17}$$

where ν denotes a frequency.

[1] S. Dushman, *loc. cit.*

[2] *Loc. cit.*

Introducing the generalized form of Einstein's photo-chemical equivalent law, we can write

$$Q_A = Nh\nu_A,$$

where ν_A represents a frequency.

As mentioned previously, this relation expresses the hypothesis that in all processes in which energy absorption or emission occurs the energy transfer occurs in multiples of a unit quantum, which is $h\nu_A$ in this case.

Now the frequency ν denotes the rate at which active molecules dissociate. It seems reasonable to expect that in some manner this frequency ought to be related to the potential energy of the constituent atoms, that is, to the heat of activation. Dushman therefore assumes that

$$\nu = \nu_A = Q_A/Nh, \tag{18}$$

so that

$$k_1 = \nu_A \epsilon^{-Nh\nu_A/RT} = \frac{Q_A}{Nh}\epsilon^{-Q_A/RT}. \tag{19}$$

Substituting for N and h, we obtain, as in case of equation (8), the relation

$$k_1 = 1.048 \times 10^{10} Q_A \epsilon^{-Q_A/RT}$$

or

$$\log k_1 = 10.0203 + \log Q_A - \frac{Q_A}{4.571T}. \tag{20}$$

This equation has been found to be in very good agreement with available data on the velocity of unimolecular reactions. Table V shows the nature of the results obtained when the equation is applied to the data of Trautz and Bandharkar on the velocity of dissociation of PH_3.

In this table, Q_A was calculated from the value of k_1 (graph) by means of equation (20). From the average of these results, $Q_A = 72{,}750$, the values of k_1 given in the last column have been calculated.

TABLE V

T	10^3k_1 (obs.)	10^3k_1 (graph.)	Q_A (calc.)	10^3k_1 (calc.)
956	22; 11; 22	18.3	72,760	17.5
953	15; 11	15.0	72,740	15.2
948	17; 10; 10; 11	12.0	72,710	12.4
945	8; 5	10.2	72,760	10.8
942	17	9.1	72,780	9.6
940	13; 14	8.3	72,740	8.9
936	2.7; 3; 8.3; 7.6; 8.7	7.1	72,730	7.6
933	12	6.3	72,690	6.6
929	5.6	5.5	72,610	5.6
923	4.4	4.6	72,560	4.4
918	3.6	3.8	72,520	3.5
845	0.54		69,920	0.113

R. C. Tolman [1] has also applied the various expressions for k_1 to the data on the rate of dissociation of N_2O_5 as determined by Daniels and Johnston [2] and finds that while all the other equations yield values which are considerably different, there is much better agreement with the observed value when equation (20) is used. Thus, for the velocity constant at $T = 338°$, the observed value is 4.87×10^{-3}, whereas that calculated by means of equation (20) is 19×10^{-3}.

Commenting upon these results, Tolman has pointed out "the theoretical improbability that the energy of activation, Q_A, can always or even usually be regarded as a constant quantity corresponding to a single frequency of radiant energy. It is well known that photo-chemical reactions are often brought about by radiant energy having a wide range of frequencies and it is also probable that molecules having themselves different internal states may require different quantities of energy for activation."

Dushman has also attempted to apply the relations deduced above for k_1 and k_2 to the calculation of equilibrium constants. Thus, let us consider the reaction $H_2 \rightleftharpoons 2H$. We assume that the dissociation is a unimolecular reaction and that the formation of molecules is a bimolecular reaction, in which combination occurs at *every collision* between hydrogen atoms. Therefore the heat of activation for the unimolecular reaction must be equal to the heat of dissociation as calculated from the temperature coefficient of the equilibrium constant by means of van't Hoff's equation.

The following table illustrates the results obtained for different reactions of the type

$$A_2 \rightleftharpoons 2A.$$

For the exact details of the calculation the reader is referred to the original paper. The last column in the table gives the value of Q calculated by means of van't Hoff's equation from the slope of $\log (K_p/\sqrt{T})$ against $1/T$, while the next to the last column gives *the value of Q calculated from the individual value of* K_p.

Langmuir and Dushman have also suggested two other applications of equation (19) which are rather important. The first application relates to the phenomenon of evaporation.[3] In a vapor which is in equilibrium with the solid (or liquid) phase, the rate of evaporation from the solid (or liquid) must be equal to that of condensation from the gas phase. According to the kinetic theory, the rate at which gas molecules at pressure p and temperature T strike a surface is given by the relation

$$n_2 = \frac{p}{\sqrt{2\pi MRT}}, \tag{21}$$

where n_2 denotes the number of mols. per cm.^{2} per sec. If we assume that

[1] *Loc. cit.*

[2] *Journ. Am. Chem. Soc.*, **43**, 53 (1921).

[3] Full details of this will be published in a joint paper in the near future.

TABLE VI

REACTIONS OF TYPE $A_2 \rightleftarrows 2A$

Reaction	$\sigma \times 10^8$	T	Log Kp	Q (calc.)	Q (obs.)
$H_2 \rightleftarrows 2H$ [1]	2.0	1200	0.3617–9	93,500	—
		1800	0.8195–4	95,450	—
		2300	0.2041–1	98,800	90,000
		3000	1.2095	101,500	—
			log K_c		
$I_2 \rightleftarrows 2I$ [2]	4.52	1073	0.1106–7	36,290	—
		1173	0.6920–7	36,460	34,530
		1273	0.1987–6	35,790	35,830
		1373	0.6395–6	36,560	36,540
		1473	0.0086–5	36,690	35,570
			log K_p		
$Br_2 \rightleftarrows 2Br$ [3]	3.74	1000	0.336–5	46,620	—
		1500	0.866 2	46,970	47,220
$Cl_2 \rightleftarrows 2Cl$ [4]	3.30	1940	0.0004–4	88,300	—
		2270	0.0043–2	82,490	120,000
		2610	0.5228–1	77,230	118,500
			log $K'p$		
$P_2 \rightleftarrows 2P$ [5]	2.85	1073	0.5441–2	49,050	—
		1173	0.3801–1	49,330	46,960
		1273	0.0792	49,450	46,540
		1373	0.6812	49,900	46,800
		1473	1.2041	50,500	47,520
$As_2 \rightleftarrows 2As$ [6]	2.79	1073	0.2041–1	46,840	—
		1173	0.9085–1	47,570	39,400
		1273	0.4983	46,550	39,080
		1373	1.0086	49,110	39,470
		1473	1.4472	49,820	39,160

[1] I. Langmuir, *J. Am. Chem. Soc.*, **37**, 418 (1915).

[2] Stock and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910). The value for σ is that given by Sackur, *Ann. Physik*, **40**, 87 (1913).

[3] Bodenstein, *Z. Elektrochem.*, **22**, 327 (1916). The original article has not been available; log K_p has therefore been calculated from the interpolation formula as given in the abstract, which is as follows:

$$\log K_p = -\frac{10{,}100}{T} + 1.75 \log T - 0.000409T + 4.726 \times 10^{-8}T^2 + 0.548.$$

[4] M. Pier, *Z. physik. Chem.*, **62**, 385 (1908). The values of K_p are calculated from his data on the degree of dissociation at the three temperatures given in the table. The value of σ is that given by Sackur (*loc. cit.*).

[5] G. Preuner and I. Brockmöller, *Z. physik. Chem.*, **81**, 129 (1913). These values of σ are calculated from the density of red phosphorus ($\rho = 2.20$).

[6] G. Preuner and I. Brockmöller, *loc. cit.* Values of σ calculated from density ($\rho = 5.73$).

there is little or no reflection of gas molecules,[1] then n_2 in equation (21) must correspond to the rate of condensation.

With regard to the rate of evaporation, we assume that the number of active molecules per unit area of surface is given by $N_0\epsilon^{-L/RT}$, where N_0 is the actual number of molecules per unit area of surface and L is the latent heat of evaporation at temperature T. Consequently, the rate of evaporation in mols. per cm.^{2} per sec. is given by

$$n_1 = \frac{N_0}{N}\nu\epsilon^{-L/RT} = \frac{N_0}{N}\cdot\frac{L}{Nh}\epsilon^{-L/RT}. \tag{22}$$

Equating n_1 and n_2, we obtain the vapor pressure relation

$$\log p = \log\left(\frac{N_0 L}{N^2 h}\right) + \frac{1}{2}\log(2\pi MRT) - \frac{L}{2.30RT}. \tag{23}$$

By means of this equation, it is obviously possible to calculate L from any individual value of p. On the other hand, L may be calculated from the slope of $\log(p/\sqrt{T})$ against $1/T$. In the following table, the latter value is given under L (obs.), while the next column shows for comparison the value of L (calc.) for a value of T which is within the range of temperature for which L (obs.) was determined from the slope. The last column gives the value of N_0 used in the calculation.

TABLE VII

Element or Compound	Range of Values of T	L (obs.)	L (calc.)	T for L (calc.)	$N_0 \times 10^{-14}$
H_2. .	14.9 20 2	212	228	18.1	5.51
He	3.23–5.25	32.0	30.1	3.97	11.4
A .	67.7–78.9	1,864	1,778	67.7	7.8
Br_2	256–332	8,100	8,210	266	5.17
Hg	283–423	14,700	16,400	333	11.2
W	2000	209,400	200,400	2000	15.85
H_2O .	223–273	11,960	9,640	258	9.72
NH_3	193–243	5,525	5,530	212	7.92
UF_6. . .	315-330	10,360	8,550	321	4.02
C_6H_6 . . .	263–393	7,484	8,428	313	3.60

The agreement is much better than that obtained by applying Trouton's law or any modification of this law. It is rather remarkable that the relation expressed by equation (23) should be found applicable to such widely different substances as helium and tungsten, even though the agreement is not exact in either case.

It will be observed that Dushman's theory is essentially an attempt to accomplish the same end as that obtained by the use of chemical constants in

[1] I. Langmuir has brought forward a great deal of evidence in favor of this view. See, especially, *Phys. Rev.*, **8**, 149 (1916).

connection with Nernst's Third Law of Thermodynamics. In both cases, the object is to evaluate the integration constant I in the relation

$$lnK = -\int_0^T \frac{Q}{RT^2}\,dT + I. \tag{24}$$

As shown by Nernst, the calculation of I may in all cases be reduced to the determination of the so-called "chemical constants" which enter into the vapor tension relation

$$\log p = -\frac{1}{4.571}\int_0^T \frac{Q}{T^2}\,dT + C. \tag{25}$$

O. Sackur [1] and Tetrode [2] showed that for a monatomic substance

$$C = \log \frac{(2\pi M)^{3/2}R^{5/2}}{N^4h^3}. \tag{26}$$

In this expression, M, the molecular (or atomic) weight, enters to the three-halves power. On the other hand, in equation (23) which was deduced from Dushman's theory, M enters to the one-half power. Furthermore, R. C. Tolman [3] and F. A. Lindemann [4] have shown, on the basis of dimensional considerations, that M must enter into the constant C (or I) with the three-halves power. Hence the fact that the unimolecular reaction velocity theory does not lead to a result in accord with well-founded conclusions regarding the dimensions of M in the chemical constant—this failure must be regarded as casting considerable doubt on Dushman's relation and the conclusions derived from it.

Rodebush has recently suggested [5] a modification of the relation for the velocity of unimolecular reaction of the following form:

$$k_R = \frac{1}{Nh}\sqrt{\frac{Q\cdot RT}{\pi}}\,\epsilon^{-Q/RT}. \tag{27}$$

Denoting the value of k in equation (19) by k_D, it follows that

$$\frac{k_R}{k_D} = \sqrt{\frac{RT}{\pi Q}}.$$

Consequently, the greater the ratio Q/T, the greater the difference between the values of k calculated by both methods. Rodebush finds that equation (27) is in very good agreement with the data on the velocity of dissociation of N_2O_5 and the rate of evaporation of mercury. The data on the velocity of dissociation of PH_3 are considered as too inaccurate, but if we apply the equa-

[1] *Ann. Physik*, **40**, 67 (1913).
[2] *Ibid.*, **38**, 434; **39**, 255 (1912).
[3] *Loc. cit.*
[4] *Phil. Mag.*, **39**, 21 (1920).
[5] *J. Am. Chem. Soc.*, **45**, 606 (1923).

tion to these data, we obtain values of k which are much smaller than those observed.

However, the same objection must be raised against equation (27) as against equation (19). Neither is in accord with the Sackur-Tetrode formula for the integration constant of monatomic substances.

A most important contribution to the discussion of this problem of unimolecular reaction velocities has been made by Christiansen.[1]

Applying the method of *a priori* probabilities used by Einstein in deriving Planck's radiation equation, "Christiansen assumes that the process of activation corresponds to the passage of a molecule by absorption of radiant energy from the normal state n to the activated state m, the difference of energy contents of these states being $E_m - E_n = h\nu$. If this difference be great, the number of molecules in the activated state under equilibrium conditions may be written

$$N_m = N \cdot \frac{P_m}{P_n} \epsilon^{-h\nu/kT},$$

where N is the total number of molecules, and P_n, P_m denote the respective *a priori* probabilities of the states in question. When chemical change is possible, an activated molecule may either revert by emission to its normal state n, or may pass by emission to another state n', the latter passage being identified with the chemical decomposition. The states m and n' are also connected by the Bohr relation

$$E_m - E_{n'} = h\nu'.$$

"According to Einstein, the probability of the change $m \rightarrow n'$ may be written equal to $(A_m{}^{n'} + B_m{}^{n'} u_{\nu'})$, where the first term is the probability of spontaneous emission, and the second is the probability of the change occurring under the action of the thermal radiation field. Hence the rate of chemical change, which is controlled by this process, is

$$k_1 = \frac{P_m}{P_n} \epsilon^{-h\nu/kT} (A_m{}^{n'} + B_m{}^{n'} u_{\nu'})$$

or, using Einstein's expression for $u_{\nu'}$,

$$k_1 = \frac{P_m}{P_n} \epsilon^{-h\nu/kT} \frac{A_m{}^{n'}}{1 - \epsilon^{-h\nu'/kT}}.$$

Christiansen now assumes that the term $A_m{}^{n'}$ which denotes the probability of the spontaneous change $m \rightarrow n'$ may be written equal to ν', the frequency characteristic of the change. With this substitution the equation reduces to

$$k_1 = \frac{P_m}{P_n} \epsilon^{-h\nu\, kT} \cdot \frac{\nu'}{1 - \epsilon^{-h\nu'/kT}}. \tag{28}$$

[1] *Z. physik. Chem.* **103**, 91 (1922).

"For the case of small values of $h\nu'/kT$ this formula approximates to

$$k_1 = \frac{P_m}{P_n} \cdot \frac{kT}{h} \epsilon^{-h\nu/kT},$$

comparable with the Herzfeld expression. For large values of $h\nu'/kT$ Christiansen shows that the formula reduces to

$$k_1 = \frac{P_m}{P_n} \cdot \nu' \cdot \epsilon^{-h\nu/kT}, \tag{29}$$

which bears a close formal resemblance to that of Dushman, the frequency ν' being, however, essentially different from that occurring in the exponential." [1]

According to Christiansen's theory, the radiation of frequency ν' which is effective in causing the transition from activated molecule to dissociation products is not necessarily the same as that frequency ν which corresponds to the change from normal to activated molecules. That is, there is no relation, on the basis of this theory, between the velocity of dissociation and the temperature-coefficient of the velocity of dissociation. On the other hand, since radiation of frequency ν' is effective in causing the dissociation, it would seem a logical consequence that the reacting substance should exhibit an absorption band for radiation of this frequency. That this conclusion is, however, not in accordance with the observations will be pointed out in a subsequent section.

A. C. McKeown [2] has modified Christiansen's arguments by omitting the assumption of the separate existence of activated molecules. Considering the two reactions $n \rightarrow m$ and $m \rightarrow n$, and applying to these reactions Einstein's arguments, McKeown arrives at the relation

$$k_1 = \frac{P_m}{P_n} \cdot \nu \epsilon^{-h\nu/kT}. \tag{30}$$

This equation differs from (19) only in the factor P_m/P_n which may be greater or less than unity. Since it is not possible at present to derive from other considerations the value of this ratio, equation (30) may obviously be brought into satisfactory agreement with any given set of observations.

It is evident from the foregoing discussion that the problem of unimolecular reactions is still far from solved, and the only method which seems to offer a solution is that suggested by Christiansen and McKeown, which is based on Einstein's theory of a priori probabilities.

Criticism of Radiation Theory: Before concluding the discussion of the relation between quantum theory and chemical reactivity, it is necessary to mention the objections which have been raised by Langmuir, Polanyi and others against the radiation theory of chemical reactions as formulated by Perrin, Lewis and Trautz.

[1] Quoted from the paper by A. C. McKeown, *Phil. Mag.*, **46**, 321 (1923).
[2] *Loc. cit.*

Langmuir has stated these objections as follows: [1]

"There are two consequences of the radiation hypothesis which should serve as a test of its validity. In the first place, it is necessary that the reacting substance shall absorb the radiation which causes the reaction. Therefore, there must be an absorption band which includes the radiation. In the second place, the total amount of energy absorbed from the radiation must be sufficient to activate the requisite number of molecules. Before any molecule can undergo reaction it must become activated and this requires the absorption of energy $h\nu$ or Q/N, an amount which can be determined experimentally for any given reaction from the temperature-coefficient of the reaction velocity." Now while Trautz, Perrin and Lewis have shown that in some cases the frequencies calculated from equation (5) agree with those of absorption bands or with the natural frequencies found from the specific heats, there are a very large number of cases in which there is no such correlation whatever. "For example," Langmuir points out, "according to Lewis's calculation, the critical frequency for the dissociation of hydrogen into atoms corresponds to a wave-length of 325 $\mu\mu$ which is in the ultra-violet region just slightly beyond the visible. There is, however, no measurable absorption of light of this frequency by hydrogen. The heats of activation for the dissociation of PH_3 and NO are 73,000 and 65,000 calories respectively. These values correspond to the wave-lengths of 392 $\mu\mu$ for PH_3 and 437 for NO, which, according to the radiation hypothesis, should lie within absorption bands. It is evident that this conclusion cannot be correct, for the above wave-lengths are in the visible spectrum, while the gases are all colorless and, therefore, do not absorb perceptible amounts of radiation in this range."

Turning to the second test, Langmuir uses the data on the rate of dissociation of PH_3. At a temperature of 948° K., the velocity constant is 0.012 per second, that is, 1.2 per cent of the phosphine present at any instant decomposes within the next second, or the average life of a molecule of PH_3 at this temperature is 83.3 seconds. One cm.^{3} of PH_3 at atmospheric pressure and 948° K. contains 1.27×10^{-5} gram-mols. The amount that dissociates in one second is, therefore, $0.012 \times 1.27 \times 10^{-5} = 1.52 \times 10^{-7}$ gram-mols.

The heat of activation (as obtained from the temperature-coefficient of the velocity) is 73,000 calories. Hence, the energy which must be supplied per cm.^{3} per second is 0.0111 calorie, or 465,000 ergs.

According to Wien's radiation law, the energy radiated per cm.^{2} per sec. between frequencies ν and $\nu + d\nu$ is given by the relation

$$E_\nu d\nu = \frac{2\pi h\nu^3}{c^2} \epsilon^{-h\nu/kT} d\nu.$$

The value of ν calculated from the energy 73,000 calories is 7.632×10^{14}, corresponding to 393.1 $\mu\mu$.

Now, while the radiation hypothesis merely assumes that the radiation is to be approximately monochromatic, Langmuir finds that even when it is assumed that all the energy below 400 $\mu\mu$ is available for activating molecules, the energy radiated is only 1.3×10^{-5} erg per sec. per cm.^{2}. "In other words, a black body at 948° K. radiates so little energy in the neighborhood of 393 $\mu\mu$ that this energy would only be sufficient to activate molecules of PH_3 in a layer having a thickness not greater than 3×10^{-11} cm., *even if all the radiation were absorbed within this layer.*"

[1] *J. Am. Chem. Soc.*, **42**, 2090 (1920).

Another objection raised by Langmuir is that, according to the radiation theory, dissociation of a gas should decrease the heat conductivity, whereas actual observation shows that the heat conductivity is increased several-fold.

Since the radiation theory fails to account for the observed rate of dissociation of PH_3, it might be assumed that the energy required for dissociation is supplied by collisions. Leaving aside for the moment the fact that, by definition, the rate of a unimolecular reaction is independent of the pressure, it is easily shown that collisions could not supply the energy required for dissociation. In the case of the dissociation of PH_3 at 948° K., the proportion of active molecules as given by the factor $\epsilon^{-73,000/1\,987T}$ is 1.6×10^{-17}. Therefore, only one collision out of 6.2×10^{16} could result in the formation of an active molecule. But, at atmospheric pressure and 948° K., each molecule of PH_3 makes only 4.2×10^9 collisions per second with other molecules. Consequently, any one molecule would become active only once every 1.5×10^7 seconds (170 days). "The average life of a molecule of PH_3 is, however, only 83 seconds (the reciprocal of the reaction velocity). The equilibrium between active and inactive molecules must, therefore, be brought about enormously more rapidly than is possible by the direct action of collisions." [1]

W. C. McC. Lewis and McKeown answer Langmuir's objections thus:

It seems to us that Langmuir is tacitly assuming photo-chemical conditions throughout. Even although he makes the temperature of the gas equal to that of the external radiation causing the reaction, he is implicitly dealing with an effect perfectly analogous to the action of radiation at a high temperature on a cold system, because he assumes that no modification is introduced as a consequence of the temperature of the gas itself. The concept of matter and radiation being at one and the same temperature means that as a result of absorption and emission among the molecules the system as a whole maintains a certain distribution of energy among all the frequencies. If by some means a set of frequencies were removed, the system would tend to make good the deficiency at the expense of all the other frequencies. The occurrence of a chemical process in the system is equivalent to the removal of a certain small range of frequencies, the removal being made good completely, provided it is physically possible to maintain the system (e.g., by means of a thermostat) at a constant temperature, i.e., provided the reaction is not too rapid. The reactions considered here belong to this class, as otherwise to speak of a velocity constant would be meaningless. Langmuir regards the velocity of a chemical process as being defined by the rate of emission of radiation from the surface of a black body, given by the expression $E_\nu\, d\nu$. This would certainly be all the energy that one would draw upon under strictly photo-chemical conditions. Under thermal conditions, however, the removal of a certain type of energy tends immediately to be made good by the system as a whole, and consequently it would seem more correct to regard the integral of $E_\nu\, d\nu$ between the limits zero and infinity as the great attainable rate at which the deficiency can be made good. Numerically, for the case of phosphine cited, this is a large quantity, of the order 10^7 ergs per second. That the actual rate of the chemical reaction is not governed by the rate of emission from a given surface, but is governed by the radiation density in the system, is shown on the basis of the following considerations. Langmuir postulates that the reaction in a one-centimeter cube of gas is to be attributed to the radiation emitted by one centimeter square of black body. If the centimeter cube of gas be distorted in such a way as to have thickness $1/x$ and face-area x square centimeters, the above postulate necessarily means that now the black body surface is x square centimeters, and hence the available energy for the cubic centimeter has been increased x times by adjustment of

[1] See R. C. Tolman, *J. Am. Chem. Soc.*, **42**, 2056 (1920), for further discussion of these objections.

the linear dimensions of the volume. Such a conclusion that the amount of thermal reaction in a given volume should depend on the special configuration of the volume is evidently fallacious.

M. Polanyi[1] has also reached the same conclusions as Langmuir regarding the untenability of any radiation hypothesis and makes the suggestion that the energy must be transmitted to the dissociating molecules by some other process.

"It seems plausible to us," he writes, "to represent this new mode of transmitting energy thus: According to our present point of view, emission of radiation consists in the coupling of a quantum transition (Quantensprung) made by an electron with a quantum transition in the ether. Similarly also, a quantum transition in a material system might be coupled with a corresponding quantum transition in another material system; for instance, a quantum change which leads to the formation of a molecule of N_2O_4 might be coupled with the quantum change which leads to the dissociation of another molecule of N_2O_4."

A somewhat similar suggestion for solving the difficulty presented by the unimolecular dissociation has been made by Langmuir:

"Unless we are to assume some new and unknown agency by which energy may be transmitted to isolated molecules, or are willing to renounce the conservation of energy, it seems necessary to conclude that each molecule must contain within itself the energy required for its own dissociation. This must be true no matter what the temperature may be. We are thus forced to assume a 'Nullpunktsenergie' or zero temperature energy. The difference between the active and inactive molecules is thus not one of total energy content, but lies rather in the availability of the internal energy for the purposes of chemical action. The exponential factor of equation (4) must then represent the probability that the energy is in a form that renders the molecule active.

"We must thus conceive of a thermal equilibrium between the electrons or other parts of a molecule, brought about by the collisions between molecules. This thermal agitation inside the molecule will presumably be governed by statistical laws and by quantum relations and will not even approximately be in accord with the equipartition law, and, therefore, the energy will be relatively small in amount. The distribution of this energy among the different parts of the molecule determines, however, the availability of the comparatively large store of zero temperature or latent energy within the molecule. According to this view it is not surprising that τ, the period during which the molecules remain active, should be small even when compared to 10^{-15} seconds.

"As far as I am aware, the above reasoning has not previously been applied to chemical reactions, although it resembles in many points some of the physical theories of radiation, photo-electric effect, etc. For example, in the theory of heat radiation it has been necessary to conceive of temperature as applying to the oscillations of single electrons in atoms. The velocity of electrons emitted in the photo-electric effect is independent of the intensity of the light, so that it has seemed necessary to assume, at least for low intensities, that the energy must have resided in the atom, and that the effect of the light is to render the energy available to the electron by some sort of trigger action. In this case, radiation plays a part analogous to that of the collisions in chemical reactions. Thus in the photo-electric effect, *the energy of the electron emitted by any atom may be very great compared to the radiant energy absorbed by that atom, although the total energy of the electrons emitted by any large surface is always less than the total energy absorbed.* Similarly, in a chemical reaction, the energy required to activate a molecule may be very great compared to the energy that is transferred to that molecule by a collision, although the total energy required for the chemical reaction in a mass of gas is always less than the total energy that is transferred by collisions, but is usually enormously greater than the total energy transferred by radiation. *Both in the photo-electric*

[1] *Z. Physik*, **1**, 337 (1920); **2**, 90 (1920); **3**, 31 (1920).

effect and in chemical reactions, it is necessary to assume a kind of trigger action by which an energy of low intensity is able to control the disposition of an energy of high intensity.

"The difficulties of explaining the photo-electric effect have seemed nearly insuperable. Planck and, later, Nernst[1] have assumed a 'Nullpunktsenergie' in order to help explain this and other phenomena. The conception of Nernst bears many resemblances to that which has been developed in the present paper. Nernst assumes, however, that the zero temperature energy owes its origin to a zero temperature radiation of great intensity which passes through all bodies without absorption, except insofar as it can be rendered available by a trigger action depending upon certain thermal changes in bodies. It hardly seems necessary to assume this zero temperature radiation to explain chemical reactions. But by doing so, we would have a new radiation hypothesis for chemical action which would be free from the objections that we have raised against the old one.

"As an illustration of the difficulties that have arisen in connection with the photo-electric effect, I may refer to a recent paper by D. L. Webster,[2] in which it is proposed to abandon the conservation of energy except as a statistical result, in order to explain some of these difficulties. Webster's reasoning can be applied with nearly equal force to the case of chemical reactions, but it seems that the assumption of a zero temperature energy which we have made above is preferable to an abandonment of the conservation of energy. The problem, however, is by no means solved, but it seems probable that the final solution will clear up both the chemical and the photo-electric problem."

It has been considered worth while to quote Langmuir rather fully because he has expressed so clearly a problem which is presented not only by the phenomena of unimolecular reactions but also by those of photo-electron emission. In fact, the difficulty extends beyond these phenomena to those presented by spectral lines, and we shall, therefore, have occasion to come back to these ideas in connection with Bohr's theory of atomic structure and the origin of spectral series.

Concluding Remarks on Unimolecular Reaction Velocities: As mentioned earlier in this chapter there is, as yet, no absolutely certain evidence for the existence of the unimolecular reactions. Nevertheless it is extremely difficult to conceive of the impossibility of such reactions. Let us consider a large mass of hydrogen in space (e.g., as a stellar atmosphere) at a definite temperature which is sufficiently high to produce a measurable amount of dissociation, as calculated from the equilibrium constant. In this case the hydrogen molecules cannot receive energy from any "walls." Yet, if we accept the kinetic point of view of equilibrium phenomena, we must assume that there exists a definite rate at which hydrogen molecules dissociate and that this is equal to the rate of combination of the atoms. In other words, a hydrogen molecule in space has an average "life" which is fixed by the temperature of the environment.

Some experiments by R. W. Wood may have an interesting bearing on this problem. As has been known for a long time, hydrogen in a discharge tube exhibits two kinds of spectra, the first a band spectrum which is white, due to molecular hydrogen, while the second is a line spectrum, which is purple and is due to atomic hydrogen. This is known as the Balmer series. Now Wood finds that the band spectrum is brought out by the presence in the

[1] *Verh. deut. Physik. Ges.*, **18**, 83 (1916).

[2] *Phys. Rev.*, **26**, 31 (1920).

discharge tube of substances which catalyze the recombination of atomic hydrogen. If such catalysts are carefully eliminated, a very intense Balmer spectrum is obtained. This means apparently that a catalyst is essential to induce the recombination of atomic hydrogen and therefore we must conclude that in the absence of such a catalyst not only would there be no formation of molecular hydrogen but there would be no dissociation.

That catalysts are essential for *all* chemical reactions seems to be a view that is gaining strength among chemists.[1] The insensitivity of dried gases to reaction, the fact that no uncatalyzed unimolecular reaction has been found, and the difficulties in the way of applying any radiation hypothesis to explain the existence of a unimolecular reaction if such a reaction ever is discovered—all these considerations would lead us to conclude that unimolecular reactions are inconceivable, a mere figment of the imagination!

Even the phenomenon of evaporation which has been regarded as a true unimolecular reaction may not actually be so, as the observations on the rise in boiling point of dust-free liquids would tend to show.

But what about the phenomenon of thermal ionization? We know from spectroscopic evidence and the recent work of Megh Nad Saha,[2] H. Norris Russell,[3] and others that in stellar atmospheres a large number of atoms are dissociated into ions and electrons, as for instance in the reaction

$$\mathrm{Na} \rightarrow \mathrm{Na}^{+} + \odot.$$

This dissociation obeys the laws of "chemical equilibria" in the same manner as if the electron were a monatomic gas. What about the rate of ionization at any definite temperature? It certainly cannot be anything else than unimolecular.

The whole problem of unimolecular reaction velocities is still open. Perhaps some light will be thrown upon it by considerations based on Einstein's theory of a priori probabilities such as have recently been suggested by E. A. Milne [4] and R. H. Fowler [5] in their discussion of the mechanism of ionization. It is of interest to point out that if their conclusions are applied to thermal dissociations we are led to velocity constants which are much less than those actually observed in the gaseous unimolecular reactions. It may therefore be that the values calculated are true for the uncatalyzed reactions while those observed are larger because of catalytic effects.

Theories of Atomic Structure

The problem of atomic structure is obviously one which may be approached from two different angles, according as the emphasis is laid on the purely

[1] Third report of National Research Council Committee on Contact Catalysis. H. S. Taylor, etc.

[2] *Phil. Mag.*, **40**, 472 (1920); *ib.*, **40**, 809 (1920); *Proc. Roy. Soc.*, A, **99**, 135 (1921).

[3] *Astrophys. Journal*, **55**, 119 (1922).

[4] *Phil. Mag.*, **47**, 209 (1924).

[5] *Phil. Mag.*, **47**, 257 (1924).

physical or on the chemical phenomena. It is therefore not surprising that the past decade has witnessed the development of two apparently different theories of atomic structure. One of these, the Lewis-Langmuir theory, has evolved from a consideration of the chemical properties of the different elements; the other, that of Bohr, represents primarily an attempt to account for the observations on spectral series, but has gradually been developed and made applicable to chemical phenomena as well. Both theories have this however in common, that they assume as fundamental hypothesis Rutherford's nuclear theory of atomic structure.

The work of J. J. Thomson and others had led to the conclusion that there exists within the atom an even more fundamental unit—the electron. It had been shown [1] that the charge on the electron is negative and has the same magnitude as that carried by a hydrogen ion in electrolysis. Thus the total electric charge per gram-equivalent weight of any ion in electrolysis has been accurately determined as 96,500 coulombs (amperes × seconds). Since we also know from kinetic theory considerations that the number of molecules per gram-molecular weight (or ions per gram-equivalent) is 6.062×10^{23}, we obtain the value of the charge on the electron,[2]

$$e = \frac{96{,}500}{6.062 \times 10^{23}} = 1.591 \times 10^{-19} \text{ coulombs},$$
$$= 1.591 \times 10^{-20} \text{ electromagnetic units},$$
$$= 4.774 \times 10^{-10} \text{ electrostatic units}.$$

Furthermore, since the ratio of the charge to the mass (e/m) was found to be equal to 1.766×10^{8} coulombs/gm., whereas in the case of a hydrogen ion this ratio is 96,500, it follows that the mass of the electron must be much smaller than that of a hydrogen atom; the most accurate determinations lead to the result that for the electron $m = 9.01 \times 10^{-28}$ or $\frac{1}{1845}$ of that of a hydrogen atom.

Since electrons are detached by X-rays from all kinds of neutral atoms, they must be common constituents of all atoms. We also find that a number of metals and oxides emit electrons when they are raised to incandescence and simultaneously made cathodes in a vacuum discharge. (Phenomenon of thermionic emission.) Furthermore, as mentioned in connection with the photo-electric effect, certain metals are able to emit electrons when illuminated by ultra-violet or even visible light.

The electron being thus a universal constituent of all atoms, the problem arises regarding the number and arrangement of the electrons in different atoms.

Scattering of α- and β-Particles by Matter and the Nuclear Theory of Atomic Structures: During the process of disintegration, radioactive elements

[1] For a full account of these investigations the reader should consult R. A. Millikan, The Electron.

[2] Actually, the charge on the electron was measured directly and the value of N was determined from the ratio $96{,}500/e$.

emit high velocity charged particles which are known as α- and β-rays respectively. It has been shown that the α-particles are identical in mass with helium atoms, but differ from the latter in carrying two units of positive electricity. On the other hand, the β-particles are extremely high speed electrons, the velocity ranging from one-tenth to nine-tenths that of light.

Observations by C. T. R. Wilson showed that when α- and β-particles are shot out from a radioactive element through a gas they travel in straight lines for fairly large distances—so large, in fact, that they must, according to all our notions based on the kinetic theory of gases, collide with an extremely large number of molecules on the way. The paths of the α- and β-particles have been photographed by C. T. R. Wilson and other observers by a very ingenious method and these photographs lead to the conclusion that β-particles must pass right through the atoms in their path until they come near enough to an electron in some atom to detach it and thus produce an ion. Similarly the α-particles traverse a large number of atoms before they are deflected, and from the observations on the directions and distribution of the paths of the deflected particles it has been shown that the cause of the deflection must be a strong field of force produced by a positive charge, which is situated within the atom, but is yet so small that the chance of being struck by an α-particle is extremely low, even though there are millions of atoms in the path of the particle.

These observations led to the view that the electrons and positive constituent or constituents of the atoms must occupy an extremely small fraction of the total volume of the atom. Practically the whole of the space occupied by an atom must be empty to an α- or β-particle.

More quantitative results regarding the actual dimensions of the positive and negative constituents of the atom were obtained as a result of experiments carried out by Geiger and Marsden in 1909–11. They observed that when α-rays are allowed to fall on a thin film of gold the majority of the particles pass through with little absorption, but occasionally, approximately one out of 20,000, a single particle is thrown back through an angle of more than a right angle. "Taking into consideration," Rutherford writes,[1] "the great energy of motion of the α-particle, such a result is as surprising as it would be to a gunner if an occasional shot at a light target was deflected back towards the gun. It was found that these large deflections must result from an encounter with a single atom. If the forces causing the deflection were electrical, it was at once evident that the electric field within the atom must be exceedingly intense. The distribution of positive electricity assumed in the Thomson atom[2] was much too diffuse to produce the intense fields required. To overcome this difficulty the writer inverted the rôle of positive electricity. Instead

[1] The Constitution of Matter and the Evolution of the Elements, Smithsonian Report for 1915, pp. 167–202.

[2] According to the theory developed by J. J. Thomson some years previously, the atom was considered as consisting of a *uniform sphere of positive electrification throughout which* the electrons were distributed uniformly.

of being distributed through a sphere comparable in size with the sphere of action of the atom, the positive electricity is supposed to be concentrated in a very minute volume or nucleus, and the greater part of the mass of the atom is supposed to be resident in this nucleus. The latter is supposed to be surrounded by a distribution of negative electrons extending over a distance comparable with the diameter of the atom as ordinarily understood. On this point of view the α-particle is the minute nucleus of the helium atom, which has lost its two external electrons. In this type of atom the large deviations of the α-particle take place when it passes through the intense electric field close to the nucleus of the colliding atom. The nearer it passes to the nucleus, the greater the deflection of the particle. Assuming that the forces between the α-particle and the nucleus of the colliding atom are mainly electrical and vary according to an inverse square law, the α-particle describes a hyperbolic orbit around the nucleus, and the relative number of α-particles deflected through different angles can be simply calculated."

Rutherford thus assumes that the scattering is due to a positive charge of magnitude Ne (where e is the unit charge of positive electricity and N is the number of these present on the nucleus) situated at the center of the atom; and that this nucleus is surrounded by N electrons uniformly distributed within a sphere of atomic radius. Furthermore, assuming the validity of the inverse square law, as mentioned already, it is possible to calculate not only the relative distribution of the α-particles for the different angles at which they are deflected, but also the minimum distance, b, corresponding to the sum of the radii of the α-particle and the colliding atom.

Geiger and Marsden showed that the actually observed distribution is in accordance with the conclusion based on the assumption of the inverse square law. Also, from their results, it may readily be shown that the radius of the nucleus of the gold atom cannot exceed 3×10^{-12} cm.—which is about one ten-thousandth part of the diameter of the atom. In the case of the scattering of α-particles by hydrogen, where the mass of the nucleus is only one fourth that of the α-particle, we would expect to find, from ordinary dynamical considerations, that some of the hydrogen atoms could be made to recoil four times as far as the penetrating distance (or range) of the α-particles. Marsden has shown that this actually occurs, and it can be calculated that, in this case, the centers of the nuclei must approach to within 10^{-13} cm. of each other. This is a smaller distance than even the diameter of the electron, which, if we assume its whole mass to be electromagnetic, is 1.88×10^{-13} cm.

Thus the nucleus, which contains practically the whole mass of the atom, is nevertheless infinitesimally small as compared with the diameter of the atom. From the observations on the disintegration of the radioactive elements during the course of which both α-particles and extremely high speed electrons are ejected, we are driven to the further conclusion that the nucleus itself is an extremely complex structure constituted of negative electrons and positive units of electricity. The simplest hypothesis and one which is in accord with all our observations is that the ultimate unit of positive electricity

is the hydrogen nucleus itself, and it has been designated in recent literature as the *proton.*

According to this view of atomic structure each element has a different nuclear charge. The scattering experiments led to the conclusion that the nuclear charge N (measured with the electronic charge as unit) was about half the atomic weight for the lighter elements, and rather less than half for the heavier. Earlier observations of C. G. Barkla on the scattering of X-rays were also found to be in accord with this conclusion. In 1913, van den Broek suggested that N probably represents also the ordinal number which determines the position of the element in the periodic table, while in 1914 Rydberg pointed out that the properties of the elements are determined not by the atomic weight, but by a number, which represents the position of the element in the periodic table. We shall, however, postpone for a subsequent section the discussion of the significance of the periodic table from the point of view of atomic structure.

It remained for Moseley (1913–14) to point out a method by which N, the nuclear charge could be determined. As the voltage over an X-ray tube is raised above a certain definite value, the anti-cathode is observed to emit an X-radiation which is characteristic of the material of the target and which is much more intense than the continuous radiation. For each element it is thus possible to obtain a series of monochromatic X-radiations. These rays as shown in Fig. 3 (which is a typical spectrum) are classified according to their wave-lengths into K, L, M, etc. Moseley carried out an investigation in which he measured the wave-lengths of the lines in the K and L series for most of the elements. He found that the spectra of the different elements, beginning with that of aluminum, and ending with that of gold, could be arranged in the same order as in the periodic table, and that under these conditions the wave-length of any one characteristic line of the K or L series *decreased regularly with increase in the ordinal number of the element in the table.* Furthermore, Moseley found that if he assigned to each element a number, N, corresponding to its place in the periodic table (Al = 13, Si = 14, etc., as far as Au = 79), there exists for each type of radiation a simple relation of the form .

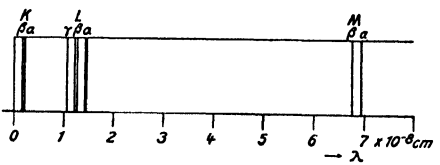


FIG. 3. K, L, M, etc., Series

$$\sqrt{\nu} = a(N - N_0), \tag{1}$$

where ν is the frequency, and a and N_0 are constants.

These measurements have been repeated and extended by de Broglie, A. W. Hull, and M. Siegbahn.[1] Fig. 4 shows the K series for some of the elements between As and Rh as photographed by the latter. The dark line

[1] M. Siegbahn has reviewed the observations on X-ray spectra and their relation to Moseley's law in *Jahrb. d. Rad. u. Elektronik*, **13**, 296 (1916).

on the extreme left hand corresponds to a wave-length zero. The first line in each spectrum is found on closer examination to consist of two lines very close together. These are known as the α_2 and α_1 lines of the K series. The darker lines to the right may also be separated into two lines, known as the

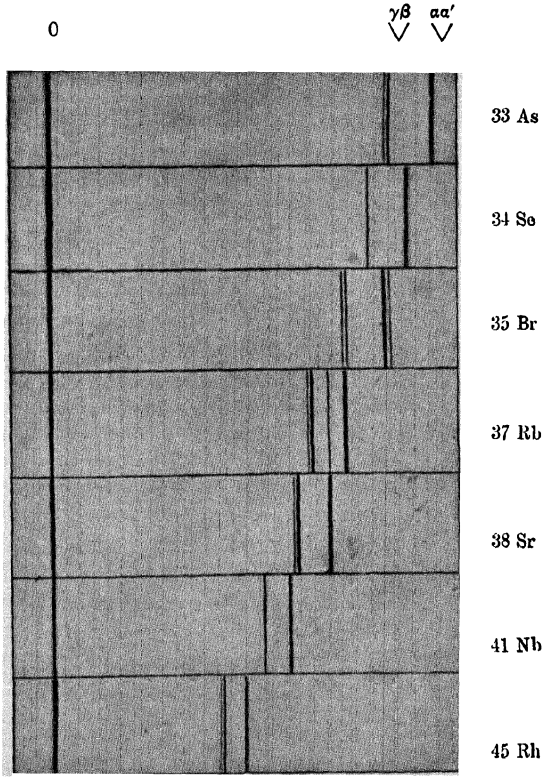


FIG. 4. K Series for Elements As–Rh

β_1 and β_2 lines of the K series. Now the significance of Moseley's law is this: If we plot the square roots of the frequency, or (what amounts to the same thing) the values of $\sqrt{1/\lambda}$ for any one of these lines, as ordinates against the ordinal number N, we obtain a straight line for each of these characteristic radiations, as shown in Fig. 5. The value of N thus determined is known as the *atomic number*. That this number also corresponds to the charge on the nucleus, has been proved definitely as a result of recent investigations in Rutherford's laboratory,[1] in which N was determined directly from careful observations on the scattering of α-particles by different substances.

[1] J. Chadwick, *Phil. Mag.*, 40, 734 (1920).

Atomic Numbers and the Periodic Arrangement of the Elements: The fact that such a relation exists which enables us to determine the atomic number, N, for each element and that this atomic number coincides in all cases with the order in which the element must be placed in the periodic table in accordance with its physical and chemical properties, must be regarded as one of the most important discoveries of the past decade.

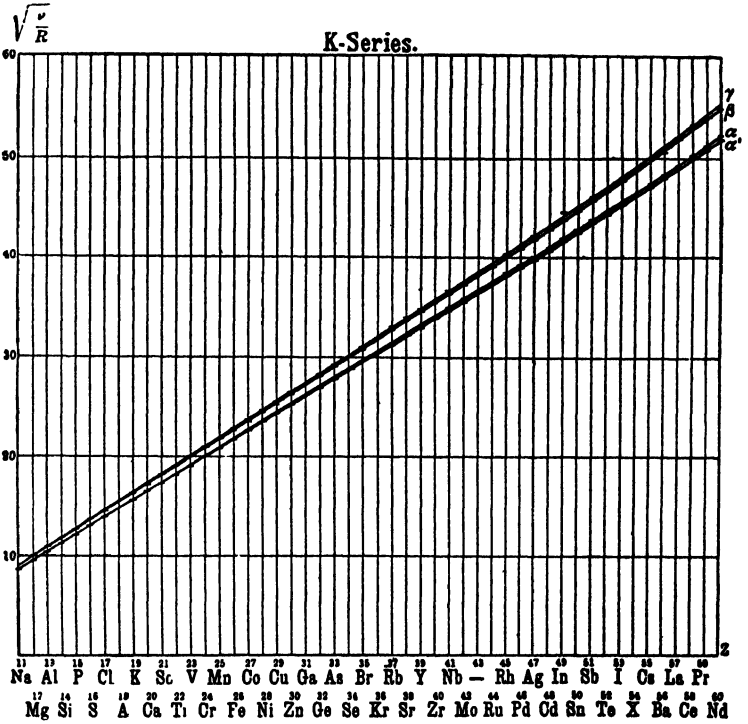


FIG. 5. Relation between Atomic Number and Frequency

To the chemist, the periodic arrangement which was first expressed clearly by Mendelejeff has been the most important guiding principle in all speculations upon atomic structure. No matter what property is considered, whether it be atomic volume, compressibility, melting point, valency, or electro-positivity (and electro-negativity), we observe a periodic variation in this function as we pass from the elements of lowest atomic weight to those of highest.[1]

That, however, the position of any element in the periodic table is not governed primarily by the atomic weight was a belief that gained greater and greater credence as the number of exceptions to the rule increased. Thus the relative positions of argon and potassium, tellurium and iodine, cobalt and nickel as determined by their chemical and physical properties are in the inverse order of their atomic weights. Furthermore, the discovery of isotopes by Aston and others has also served to emphasize the relative unimportance of atomic weight as compared with atomic number. As well known, it was first shown in the case of radio-

[1] W. D. Harkins and R. E. Hall have written an interesting and full discussion of the periodic system in *J. Am. Chem. Soc.*, **38**, 169 (1916).

active elements and subsequently found to be also true for a number of other elements that we may have elements of the same atomic number but different atomic weights. Such elements, since they occupy the same place in the periodic arrangement, are known as *isotopes*. In all their chemical properties and all physical properties (except these which depend upon *mass* and radioactive properties), the isotopes corresponding to any given atomic number are identical, yet the atomic masses are different.

These facts lead to the conclusion that the charge on the nucleus, or atomic number, governs all the physical and chemical properties of the atom (except, of course, the radioactive and gravitational properties which depend upon the structure and mass of the nucleus itself).

Furthermore, in order to account for chemical combination and periodic properties, we must assume that the electrons arranged around the nucleus possess different functions according as they belong to the outer or inner set. The outer electrons are active in chemical combination and conduction of electricity through metals. They also must give rise to the ordinary emission spectra which we know are similar for elements of the same group in the periodic arrangement. The number of electrons in this outer set must undergo periodic change in distribution and number as N increases.

On the other hand, the inner electrons are unaffected by ordinary chemical operations, but high velocity electrons (such as cathode rays) may stimulate them and thus produce the high-frequency spectra observed by Moseley and others. As pointed out by Kossel,[1] the fact that for any one type of monochromatic X-radiation (such as the $K\alpha_1$ line) the frequency varies in a regular manner from elements of low atomic number to those of highest shows that the periodicity observed in the outer electrons does not extend to the innermost.

Atom Model of Lewis and Langmuir:[2] As mentioned previously, this theory is based on evidence furnished by a study of the chemical properties of the elements and their relationships as shown by the Periodic Table. To the chemist, the most striking phenomenon exhibited by the different atoms is the periodic change in valency and electron affinity. The old belief in the existence of "bonds," an idea which has been found so extremely useful in the domain of organic chemistry, has necessarily governed the fundamental assumptions of the new theory. With electrons located in definite arrangements in the atomic structure, it is possible to account in a simple manner for chemical data. As to whether such a *static atom* (in contradistinction to Bohr's dynamic atom) is electrically stable, is not a matter of primary consideration from the chemist's point of view.[3]

" Cubical " Atom of G. N. Lewis. Nature of Chemical Bond: In 1916, G. N. Lewis[4] suggested "what may be called the theory of the cubical atom." The main features of this theory are as follows:

[1] *Ann. Physik*, **49**, 229 (1916).

[2] For review of earlier theories of atomic structure and references to these the reader is referred to the paper by S. Dushman, *Gen. Electric Rev.*, 186, 397 (1917).

[3] Langmuir has, however, attempted to postulate laws of force between the electrons and nucleus which lead to some of the more striking quantitative relations deduced by Bohr. Reference to this is made in a subsequent section.

[4] *J. Am. Chem. Soc.*, **38**, 762 (1916). The ideas contained in this paper have since been expanded by Prof. Lewis in his book on Valence and the Structure of Atoms and Molecules, The Chemical Catalog Co., 1923.

Assuming Rutherford's conclusions on the nuclear structure of the atom and that the number of electrons in each atom corresponds to the ordinal position of the element in the periodic table, it is further postulated that groups of two or eight electrons are exceedingly stable. This accounts for the chemical inertness of the elements of Group *O*. The atom of helium contains two electrons; that of neon consists of a pair of electrons (as in helium) inside a cube of eight electrons. In the case of argon, the eight additional electrons arrange themselves at the corners of a cube which is external to the neon cube. Furthermore, the atom of every other element tends to take on or give up electrons so as to resemble either helium or one of the other elements of the inert group. Thus, lithium, which contains one electron outside the helium pair, tends to give up this extra electron and is, therefore, electro-positive in its chemical properties, while fluorine, since it lacks only one electron to form a cube like that of neon, is extremely electro-negative. Hence, when lithium reacts with fluorine, an electron is transferred from the former to the latter, resulting in the formation of Li^+F^-. Similarly, the atom of sodium tends to form Na^+ by giving up the electron which is external to the neon cube.

But the tendency of every atom towards an arrangement of electrons with eight in the outermost shell is satisfied not only by the *transfer* of an electron from the shell of one atom to that of another, it is also satisfied by the *sharing* of one or more pairs of electrons by two atoms.

As Lewis states,[1] "The discovery that these electrons, which are held jointly by two atoms, always occur in pairs led to the realization that the 'rule of two' is even more fundamental than the 'rule of eight.' We see, at the beginning of the periodic table, that helium with its pair of electrons has the same qualities of stability that characterize the remaining rare gases which possess outer octets. Hydrogen may form hydrogen ion with no electrons, it may form hydride ion by adding one electron and thus completing the stable pair,[2] or finally two hydrogen atoms may unite to form the hydrogen molecule, in which each atom shares with the other a pair of electrons.

"I called particular attention (in the 1916 paper) to the remarkable fact that, when we count up the electrons which are comprised in the valence shells of various types of molecules, we find that, of some hundred thousand known substances, all but a handful contain an even number of such electrons. It is therefore an almost universal rule that the number of valence electrons in a molecule is a multiple of two."

After pointing out that the *odd* molecules, that is, those containing an uneven number of valence electrons, are mostly intensely colored and highly paramagnetic, Lewis gives the following definition of the *chemical bond* in terms of his theory:

"Two electrons coupled together, when lying between two atomic centers, and held jointly in the two atoms, I have considered to be the chemical bond.

[1] Valence, p. 79.

[2] Lewis refers here to the interesting observation (Bardwell, *J. Am. Chem. Soc.*, **44**, 2499 (1922)) that electrolysis of a hydride causes the evolution of hydrogen at *the anode*.

We thus have a concrete picture of that physical entity, that 'hook and eye' which is part of the creed of the organic chemist."

Thus, two chlorine atoms in forming a molecule share one pair of electrons, while two oxygen atoms share two pairs, and in the case of methane, the carbon atom shares four pairs of electrons with the hydrogen atoms.

On the basis of this theory Lewis has been able to account satisfactorily for the existence of *polar* and *non-polar* types of chemical substances. Potassium chloride is typical of the extremely polar, while methane may be regarded as a representative of the non-polar compounds.

"The pair of electrons which constitutes the bond may lie between two atomic centers in such a position that there is no electric polarization, or it may be shifted toward one or the other atom in order to give to that atom a negative, and consequently to the other atom a positive, charge. But we can no longer speak of any atom as having an integral number of units of charge, except in the case where one atom takes exclusive possession of the bonding pair, and forms an ion.

"For example we may suppose that the normal state of the hydrogen molecule is one in which the electron pair is symmetrically placed between the two atoms. In sodium hydride, on the other hand, we may regard the bonding pair as lying nearer to the hydrogen than to the sodium, *making the hydrogen negative;* while, in hydrochloric acid, the bond is shifted toward the chlorine, leaving the hydrogen with a positive charge. In the presence of a polar solvent the chlorine assumes full possession of the bonding pair, and we have complete ionization. I attempted to represent these displacements of electrons by such formulæ as

$$H:H, \qquad Na:H, \qquad H:\ddot{\underset{\cdot\cdot}{Cl}}:, \qquad [H^+] + [:\ddot{\underset{\cdot\cdot}{Cl}}:^-].^1$$

"Even a symmetrical molecule like that of H_2 or I_2 may, from time to time, become polarized in one direction or the other, as a consequence of the disturbance due to thermal motion. When iodine vapor is heated to a high temperature, the molecule breaks in such a way as to sever the bonding pair, and forms two uncharged iodine atoms. On the other hand, in liquid iodine, a few of the molecules break apart in another manner. The bonding pair remains intact but remains the exclusive property of one atom, forming I^+ and I^-. These two types of dissociation may be represented as follows:

$$:\underset{\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot}{I}}:\underset{\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot}{I}}: = :\underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}. + .\underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}: \qquad :\underset{\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot}{I}}:\underset{\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot}{I}}: = :\underset{\cdot\cdot}{\overset{\cdot\cdot}{I}} + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}:$$

In other molecules, some displacement of electrons may occur without full ionization, thus making the molecule more or less polar.

"Bromine, chlorine, fluorine and hydrogen, in the order named, show a diminishing tendency toward either of the above types of dissociation. We

[1] In this and subsequent electronic formulæ, only the outermost electrons are indicated.

say that the bond in the iodine molecule is looser than the bond in the chlorine molecule. We also say that iodine is a more polar substance than bromine.

"The two ideas are not synonymous, but, as a rule, the molecule is less polar the tighter the bond. Professor Branch has called my attention to a certain ambiguity in this regard. When we speak of a polar substance or a polar molecule, we imply either that the molecules are largely polarized or that they are readily capable of polarization. In other words, we imply that the bonding pair is either displaced in one direction or the other, or that it is easily displaceable, in which case we may say that the pair is mobile. The two things ordinarily go together, but this is not invariably so. The molecule of sodium chloride is highly polarized, but the electron pair is so tightly held by the chlorine atom as to possess little mobility."

Langmuir's Extension of Lewis' Theory: While Lewis had confined his attention mainly to the elements of lower atomic number (the first 35 approximately), Langmuir has extended the same conception to the other elements of the periodic table.[1]

"In attempting to determine," Langmuir states, "the arrangement of electrons in atoms, we must be guided by the numbers of electrons which make up the atoms of the inert gases; in other words by the atomic numbers of these elements, namely, helium 2, neon 10, argon 18, krypton 36, xenon 54, and niton 86."

Rydberg [2] has pointed out that these numbers are obtained from the series

$$N = 2(1 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 +).$$

Presumably, therefore, there is something about an arrangement involving 2×3^2 or 2×4^2 electrons which makes this just as stable as the cube in the case of neon and argon. Therefore, Langmuir assumes that the outer shells of the atoms of krypton and xenon each contain 18 electrons, while $2 \times 4^2 = 32$ electrons are required to complete the outer shell of the niton atom.

Langmuir has presented his suggestions on atomic structure and chemical combination in the form of eleven postulates. The first seven of these deal with atomic structure, and the last four with the formation of chemical compounds. He assumes that the electrons are distributed through a series of concentric shells, and, in the case of the inert gases, the electrons are arranged in each shell symmetrically about a plane passing through the nucleus. The first or innermost shell contains two cells, the second contains 8, the third 18, and the fourth 32. Furthermore, while each of the innermost cells can contain only one electron, each of the other cells is capable of holding two. The existence of the factor 2 in Rydberg's series necessitates the assumption of symmetry about an equatorial plane, while the fact that 2^2 and 3^2 each occur twice leads to the assumption that two electrons may occupy one cell. Langmuir states "we may assume that two electrons occupying the same cell are at different distances from the nucleus. Each shell, containing its full quota

[1] *J. Am. Chem. Soc.*, **41**, 868 (1919), and subsequent papers.

[2] *Phil. Mag.*, **28**, 144 (1914).

of electrons, thus consists of two layers." These layers are referred to by the symbols I, IIa, IIb, IIIa, IIIb and IVa, where the Roman numerals denote the shell containing the layer.

On the basis of these postulates, Langmuir derives the atomic structures for the different elements, shown in Table VIII.[1]

TABLE VIII

ARRANGEMENT OF ELECTRONS IN ATOMS (ACCORDING TO LANGMUIR)

N:	1	3	11	19	37	55	87
Layer:	I	IIa	IIb	IIIa	IIIb	IVa	IVb
Group I....	H 1	Li 1	Na 1	K 1	Rb 1	Cs 1	— 1
II. .		Be 2	Mg 2	Ca 2	Sr 2	Ba 2	Ra 2
III		B 3	Al 3	Sc 3	Y 3	La 3	Ac 3
IV ..		C 4	Si 4	Ti 4	Zr 4	Ce 4	Th 4
						Pr 5	
						Nd 6	
						— 7	
						Sm 8	
						Eu 9	
						Gd 10	.....Rare Earths
						Tb 11	
						Dy 12	
						Ho 13	
						Er 14	
						— 15	
						Yb 16	
						Lu 17	
						Hf 18	
V...				V 5	Cb 5	Ta 19	Ux_2 5
VI ..				Cr 6	Mo 6	W 20	U 6
VII .				Mn 7	— 7	— 21	
				Fe 8	Ru 8	Os 22	
VIII .				Co 9	Rh 9	Ir 23	
				Ni 10	Pd 10	Pt 24	
I..				Cu 11	Ag 11	Au 25	
II..				Zn 12	Cd 12	Hg 26	
III				Ga 13	In 13	Tl 27	
IV .				Ge 14	Sn 14	Pb 28	
V...		N 5	P 5	As 15	Sb 15	Bi 29	
VI .		O 6	S 6	Se 16	Te 16	RaF 30	
VII		F 7	Cl 7	Br 17	I 17	— 31	
0 .	He 2	Ne 8	Ar 8	Kr 18	Xe 18	Rn 32	

[1] The form of the table differs somewhat from that given by Langmuir (*J. Am. Chem. Soc.*, **41**, 874 (1919)). Furthermore, in the case of the rare earths, use has been made of the revised arrangement as given by N. Bohr and D. Coster, *Z. Physik*, **12**, 342 (1922), also *Naturwissenschaften*, **11**, 606, 567 (1923).

The different elements are arranged so that elements with outer electrons in the same layer occur in the same column. Lewis and Langmuir have distinguished between the shell or valence layer of electrons in an atom and the *kernel.* The kernel consists of the nucleus and the inner electrons, which do not play any rôle in chemical combination. Thus, lithium atom consists of a shell of one electron and a kernel of unit positive charge (nuclear positive charge of three less the negative charge on the two electrons in layer I). Similarly magnesium atom consists of a shell of two electrons and a kernel of net positive charge of two units.

Although more recent developments have led to considerable modification in our conceptions of the arrangement of electrons in the kernels of elements of higher atomic number (above Ca, $N = 20$), nevertheless, it is worth while discussing, to some extent, Langmuir's views on the structures of the different elements.[1]

Arrangement of Electrons in First 18 Elements: In the case of the first 18 elements (hydrogen to argon) the structure of the atom is governed by the generalization which, as mentioned already, Lewis emphasized, that groups of two electrons or eight electrons are extremely stable. Thus helium forms a kernel about which are built up the next eight electrons until neon is reached. This in turn forms a kernel about which eight more electrons can be arranged in a third shell until the stable arrangement is reached which corresponds to argon. The elements intervening between helium and neon either give up electrons (Li, Be), in which case they revert to the stable structure of helium, or take up electrons (O, F), in which case they assume the same structure as that of neon. Carbon forms an octet by sharing its four electrons with other atoms, and the four "bonds" are represented by four pairs of electrons arranged around the kernel, which, in the case of the elements of this period, is represented by the two electrons in the first layer and the nucleus.

With sodium, we begin a third layer and the kernel may be represented by the electronic arrangement (2, 8). Hence, sodium resembles lithium in having a single electron in the outer shell, and shows the same electro-positive properties. The remaining elements of the period resemble, in regard to the structure of the outer shell, the corresponding elements of the lithium-neon period.

First Long Period: The distribution of electrons in argon is represented by 2, 8, 8, and, reasoning by analogy with the elements of the preceding period, we would expect to find that potassium resembles lithium and sodium, that calcium resembles beryllium and magnesium, and so forth. Actually, we find that this resemblance extends strictly only to the first three elements, that is, up to and including scandium ($N = 21$). The explanation, according to Langmuir, is that it requires eighteen electrons to complete each of the layers IIIa and IIIb, and, consequently, certain new factors have to be taken into account. "The electrons in the outside layer tend to line themselves up (in

[1] In this discussion we have followed rather closely the remarks by Langmuir in his original paper (*J. Am. Chem. Soc.*, **41**, 868 (1919)).

a radial direction) with those of the underlying shell because of a magnetic field probably always to be associated with electrons bound in atoms. This attraction may be more or less counteracted by electrostatic repulsion between the outside electrons and those in the underlying shell. The electrons in the outside layer also repel each other and thus tend to distribute themselves among the available cells so as to be as far apart as possible. The actual positions of equilibrium depend on a balance between these three sets of forces together with the attractive force exerted by the nucleus.

"When the number of electrons in the outside layer is small, the magnetic attraction excited by the electrons of the inner shells tends to predominate over the electrostatic repulsion, but, when the atomic number and the number of electrons in the outside layer increase, the electrostatic forces gradually become the controlling factor. As a result, when there are few electrons in the outer layer, these arrange themselves in the cells over those of the underlying shell, but, where the outside layer begins to approach its full quota of electrons, the cells over the underlying electrons tend to remain empty.

"The electro-positive character of the first three elements of this period (K, Ca, and Sc) is determined by the ease with which they revert to argon. Elements like vanadium, chromium and manganese, however, cannot form positive ions by reverting to argon, for they would have to give up completely 5, 6, and 7 electrons, respectively. The large electrostatic forces involved prevent the formation of ions with such large charges. The electro-positive character of these elements must manifest itself, therefore, by the formation of ions with fewer charges."

In the case of iron only eight out of the eighteen outside cells are occupied by electrons. This atom, therefore, does not have the same stability as neon or argon, and there is little tendency for the elements of lower atomic weight to take up electrons. These elements form oxides in which the electrons are shared with oxygen atoms.

The structure which we can assign to iron on the basis of the above considerations is as follows: Owing to the magnetic forces between electrons in the outer layer and those in the layer underneath, the electrons will tend to arrange themselves symmetrically along the corners of three concentric cubes with two electrons (corresponding to the helium structure) in the center. "In cobalt and nickel whose atomic numbers are, respectively, one and two units larger than that of iron, the *extra* electrons can no longer be arranged over those in the underlying shell." Therefore, they go into the polar axis of the atom.

"The present theory thus explains in a perfectly satisfactory way the anomalous position of iron, cobalt and nickel in the periodic table. We shall see that it also accounts for their unusual magnetic properties.

"The ordinary chemical properties of these three elements resemble those of chromium and manganese, except that they have lost most of the acid-forming properties, because they are so far removed from argon that they cannot revert to it. Thus, these three elements never show valences of 8, 9, and 10 and do not form acids corresponding to chromates and permanganates.

They form, predominantly, salts in which they exist as divalent or tervalent cations, and for the same reasons as those discussed in connection with vanadium, chromium and manganese. The colors of their salts are even more marked than those of the chromium and manganese cations which indicates that their electrons are even more loosely bound. With nickel the number of electrons is so great that the electrostatic forces seriously oppose the magnetic forces. The introduction of the electrons in the polar axis also tends to force the other electrons away from their positions over the underlying electrons and thus still further weakens the magnetic forces. The effect is thus to bring about a rearrangement of the electrons so that the square containing the four electrons in each hemisphere tends to revolve 45° about the polar axis. This arrangement, which we may call the β-form, has a higher degree of symmetry than the α-form previously considered, in that all the electrons in the β-form are as far from the underlying ones as possible, while in the α-form one electron was far from, and the other four were close to, the inner ones.

"The β-form of the nickel atom has a symmetry which exceeds that o any other atom between argon and krypton, with the possible exception of iron. Thus the atoms of the elements above nickel in giving up electrons tend to revert to either nickel or iron. But, by the time we get to elements above nickel, the large nuclear charge causes the electrostatic forces to predominate over the magnetic, so that the tendency to revert to iron is eliminated.

"As a matter of fact, we find that copper (cuprous) has a valency of 1, zinc has 2, gallium 3, etc., right up to selenium, 6. These elements therefore all tend to give up electrons in such a way that their atoms revert back to the symmetrical β-form of the nickel atom. It must be remembered that after these atoms have given up their extra electrons their outside layers contain the same number of electrons as the nickel atoms but they differ from the latter in that the charge on the nucleus is greater and therefore there is a much greater tendency for the β-form to be the more stable form.

"In the case of copper we find that the ability to form an ion having an α-form is now wholly lost. Thus, copper forms divalent ions. The cupric ions form a continuation of the family of similar elements which extended from vanadium to nickel, but the cuprous salts form a radical departure from this series. The electrons are given up in the formation of cupric ions not because there is any inherent stability in the cobalt atom to which it reverts but for the same reason that chromium, manganese, iron, nickel and cobalt form divalent ions. It is interesting to note that the cupric salts are highly colored and in many ways resemble nickel salts. The cuprous salts on the other hand resemble those of no element thus far considered. It is true the atoms have the same valences as those of the alkali metals and that the ions are colorless in both cases, showing that all electrons are firmly held. But the solubilities of the salts are very radically different. Now, this is just the kind of difference we should expect from the difference between the structure of Niβ and the atoms of the inert gases. The atoms of these gases are characterized by weak secondary valence forces (low boiling points, etc.), whereas atoms having only

about half of the cells in the outside shell filled have strong residual fields of force. The properties of the alkali metals are therefore determined almost wholly by the electrostatic charges on their ions, but with ions like that of univalent copper there is, in addition, the residual field of force due to the large number of unsaturated electrons. The cuprous ion thus tends to form insoluble solid salts and many addition products.

"With zinc we have completely broken away from the tendency to variable valence. The salts are now all colorless. The tendency to form molecular compounds (secondary valence) still distinguishes this element from the more purely electro-positive metal like calcium.

"Germanium is interesting since it begins to acquire an electro-negative character because of its ability to assume the form of krypton by taking up 4 electrons. It thus resembles carbon and silicon in forming a volatile hydride whereas such a tendency is absent in case of titanium.

"In arsenic, selenium, and bromine, because of the proximity of krypton, the electro-negative character predominates and these elements thus closely resemble phosphorus, sulfur, and chlorine. But their tendency to form insoluble secondary valence products distinguishes them from these other elements."

Second Long Period and "Rare Earth" Group: When we come to the second long period (rubidium to xenon), we naturally find a repetition of the atomic structures assigned to the atoms of the preceding period, so that palladium has two electrons in the polar axis and exhibits α- and β-forms as in the case of nickel.

After xenon, the fourth shell begins and, since there are thirty-two cells to be filled by electrons, we should expect to find a large number of elements with very similar properties and similar valencies. The first four elements show electro-positive character because of their tendency to revert to xenon. As more electrons are added they tend to arrange themselves symmetrically over the eighteen electrons in layer IIIb and it is interesting to observe that the eighteenth element from xenon corresponds to the last element of the "rare earth" group, hafnium, which was discovered within the past two years by D. Coster and von Hevesy.

Thus, Langmuir's theory accounts satisfactorily for the exact number of the rare earth elements and their properties. "Since the forces holding these eighteen electrons are predominantly magnetic and since the constraints are not of the rigid kind characteristic of the inert gases, we should expect these elements to be paramagnetic. As a matter of fact, the rare earths are the most strongly paramagnetic of any of the elements except those from manganese to nickel.

"By the time the eighteen electrons have been added, the electrostatic forces have begun to oppose the magnetic attraction to a marked degree. Therefore, when, in tantalum, an additional electron is added, the whole outside shell tends to rearrange itself so that the empty cells will come opposite the electrons of the underlying shell. The most symmetrical arrangement of this

kind will occur when there are eighteen empty cells opposite the eighteen underlying electrons. The atomic number of niton (radon) in which the fourth shell is complete is 86—therefore an element having eighteen empty spaces in the fourth will have an atomic number 68 corresponding to erbium. The structure of this β-form of erbium has the same kind of stability for large nuclear charges that we found in the cases of β-nickel and β-palladium. We may therefore expect that the atoms beyond holmium will show a marked tendency to revert to β-erbium. Thus tantalum with an atomic number 73 tends to lose five electrons and tungsten to lose six. The properties of tantalum and tungsten thus resemble those of columbium and molybdenum, but, because of the complexity of the atom to which they revert, and in general because of the large numbers of electrons in their outside shell, their secondary valence forces are more highly developed.

"The β-form of the erbium atom contains eighteen empty cells arranged over the eighteen cells of the third shell. When electrons are added, as we pass to elements of large atomic number the first eight of them naturally tend to arrange themselves at the corners of a cube, because of the magnetic attraction of the eight electrons in the second shell. The next two electrons, for reasons of symmetry, then arrange themselves in the polar axis. We thus have the three 'eighth group' elements osmium, iridium and platinum. Because of the weakness of the forces acting between the fourth and the second shell we should not expect strongly developed magnetic properties in these elements. As a matter of fact, osmium and iridium have susceptibilities nearly equal to zero, but there is a small but sharp rise at platinum making this element about one fourth as paramagnetic as palladium. The next elements gold, mercury, etc., are distinctly diamagnetic. The same sharp break occurs here as we found between nickel and copper, palladium and silver, lutecium and tantalum, although its magnitude is much less. We may therefore assume that beyond platinum the electrons tend to rearrange themselves in a β-form in which the ten electrons, that have been added since erbium, endeavor to get farther away from those of the underlying electrons. The eight empty cells tend to take symmetrical positions in the atom probably at corners of a cube, and the cells containing electrons space themselves as best they can. The fact that an arrangement of this kind does not have nearly the symmetry which we found for the β-form of the nickel atom is probably the explanation of the fact that the tendency of the succeeding elements to revert to this β-form of platinum is much less marked than we observed in the cases of reversion to nickel, palladium and erbium. Thus, we find that gold and mercury have variable valence, differing in this respect from silver and cadmium. Thallium forms univalent and tervalent ions whereas indium forms only tervalent. Lead only exceptionally is quadrivalent, while this seems to be the normal condition of tin compounds. Thus, stannous salts are strong reducing agents, but divalent lead salts are not. Bismuth is normally tervalent and forms only a few very unstable compounds in which it is quinquivalent. Antimony, on the other hand, has about equal tendencies to be tervalent or quinquivalent."

Lewis-Langmuir Theory of Valence and Chemical Combination: Mention has already been made of Lewis's conception of the nature of the chemical bond. The stability of two electrons in helium and of eight electrons in neon and argon is considered by both Lewis and Langmuir as of fundamental importance in governing the formation of chemical compounds. The latter has designated the stable group of eight electrons the "octet" and the theory of chemical combination which we shall discuss in the following section is known as the "octet theory of valence."

Langmuir has stated this theory in the form of the following four postulates:[1]

"*Postulate 1.* The very stable arrangements of electrons corresponding to those of the inert gases are characterized by strong internal but unusually weak external fields of force. The magnetic and electrostatic forces are each very nearly internally balanced. The smaller the atomic number of the element the weaker are these external fields.

"*Postulate 2.* The pair of electrons in the helium atom presents the most stable possible arrangement. A stable pair of this kind forms only under the direct influence of positive charges.

"The positive charges producing the stable pair may be:

"(*a*) The nucleus of any element.

"(*b*) Two hydrogen nuclei.

"(*c*) A hydrogen nucleus together with the kernel of an atom.

"(*d*) Two atomic kernels.

"These are listed in the order of their stability.

"*Postulate 3.* After the very stable pairs (Postulate 2) the next most stable arrangement of electrons is the group of eight such as forms the outside layer in atoms of neon and argon. We shall call this stable group of eight electrons the *octet.* Any atom up to argon having more than two positive charges on its kernel tends to take up electrons to form an octet. The greater the charge on the kernel the stronger is this tendency. In exceptional cases, the octet can form about a complex kernel, that is, about a structure containing the kernels of two atoms bound together by a pair of electrons (Postulate 2).

"*Postulate 4. Electrons Held in Common.*—Two octets may hold one, two or sometimes even three pairs of electrons in common. A stable pair and an octet may hold a pair of electrons in common. An octet may share an even number of its electrons with one, two, three or four other octets. No electrons can form parts of more than two octets."

It will be recognized that these postulates form a logical extension of the conceptions at which Lewis had arrived in considering polar and non-polar compounds. Applying these postulates to chemical combination, Langmuir derives a theory of valence which he states as follows:

"Let c be the total number of *available electrons* in the shells of the atoms forming a given molecule. Let n be the number of octets formed by their combination and let p be the number of electrons held in common by the

[1] These are Postulates 8–11 in the original paper.

octets. For every pair of electrons held in common there is a saving of 2 in the number of electrons needed to form the octets. Thus we have

$$e = 8n - 2p. \tag{2a}$$

"For most purposes it is more convenient to use this equation in the form

$$p = \tfrac{1}{2}(8n - e). \tag{2b}$$

"When a hydrogen nucleus holds a pair of electrons in common with an octet, this pair should not be counted in determining the value of p, since it does not result in any saving in the numbers of electrons required to form the octets."

Now, let us see how these equations apply to different cases of chemical combination.

Water (H_2O): In this case $n = 1$, $e = 8$ (6 for the oxygen and one for each hydrogen). Hence $p = 0$. "This means that no electrons are held in common between octets, which must obviously be the case for any molecule containing only one octet. The fact that we found $p = 0$ thus shows that the compound H_2O can exist. The two hydrogen nuclei attach themselves to two pairs of electrons forming the octet. The arrangement is presumably as illustrated in Fig. 6. The hydrogen nuclei are represented by the + signs and the electrons in the octet by the small circles while the nucleus of the oxygen atom is shown as a black circle."

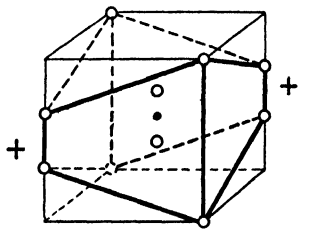


FIG. 6. Diagram of the Water Molecule

We may also represent this molecule two-dimensionally by the formulæ

$$\mathrm{H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H}, \qquad \text{or} \qquad \mathrm{H : O : H}.$$

In the second mode of representation we merely show that the oxygen atom shares two pairs of electrons with hydrogen atoms. Thus, the pair of electrons takes the place of the single bond in the conventional formula H − O − H.

Oxygen and Ozone: For every oxygen atom we must have an octet. Let us therefore assume $n = 2$, then since $e = 2 \times 6$, it follows that $p = 2$. Hence O_2 will be represented by the formula O = O, showing that two pairs of electrons are held in common. In the case of ozone, O_3, $n = 3$, and since $e = 3 \times 6$, $p = 3$. The formula

$$\mathrm{O = O - O}$$

shows that three pairs of electrons are held in common by the three octets. Presumably we could obtain a molecule O − O = O − O, but, as well known, this is not stable.

In these formulæ it is to be remembered that each bond represents a pair of electrons held in common by the two octets. It has only a formal resemblance with the classical formulæ in which each bond corresponds to a single valency. The two methods of representation agree in certain cases, like that of O_2 and H_2O, and CO_2, CH_4 and organic compounds in general. But *the main value of the octet theory consists in the fact that it gives a rational explanation for the structures of a large number of inorganic compounds without recourse to the assumption that the same atom may exhibit different valencies in different compounds.* This point will be illustrated better by the cases discussed below.

Carbon Dioxide (CO_2): Since $n = 3$, and $e = 4 + (2 \times 6)$, $p = 4$. Hence, the formula is

$$O = C = O.$$

Langmuir has shown how the theory applies to hydrocarbons by attempting to deduce on the basis of the octet theory what substances of the general type C_xH_y can exist. Since in all octet compounds there must be an even number of electrons (otherwise p would be a fractional number), it follows that in all hydrocarbons there must be an even number of hydrogen atoms, and hence the general formula may be represented by C_xH_{2y}.

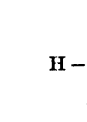
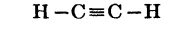
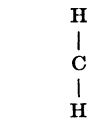
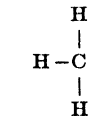
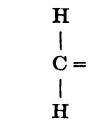
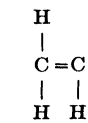
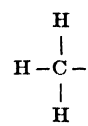
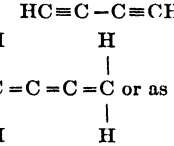
In Table IX, the first column gives the empirical formula of the hypothetical compound. The values of n and e are given in the next two columns, while p, calculated by equation (2), is given in the fourth column. The last column gives the resulting structural formula which may be assumed to represent the molecule.

In all these cases, the old theory gives the same structures as those given by the new theory. However, it must be noted that the old theory of valence was developed around the chemistry of carbon compounds. It is when we come to discuss such cases as those of the compounds of nitrogen and oxygen that the valence theory fails while the new theory becomes a safe guide in deducing the possible compounds. Since nitrogen has five electrons in its shell and oxygen has six, it is evident that the compounds must have the general formula N_2O_x. Applying the octet theory, we obtain the series shown in Table X.

Structure of Nitrogen Molecule, Carbon Monoxide, Nitric Oxide, and Hydrocyanic Acid: "If we apply the octet theory to the nitrogen molecule, by placing $n = 2$, $e = 10$, we find $p = 3$. We are thus led to the formula $N \equiv N$ for the nitrogen molecule. Now, in acetylene we have an illustration of two atoms holding three pairs of electrons in common. Such a substance is endothermic, forms additional products easily, and even by itself is relatively unstable. A structure of this kind could not possibly account for the properties of nitrogen."

Langmuir points out that in most of its properties elementary nitrogen resembles argon. Its freezing point lies between those of argon and oxygen, while its boiling point lies below those of either of these gases. The nitrogen molecule must, therefore, have a weaker external field of force than either that

TABLE IX

	n	e	p	Constitution
CH_2	1	6	1	Impossible
CH_4	1	8	0	
CH_6	1	10	−1	Impossible
C_2H_2	2	10	3	
C_2H_4 .	2	12	2	
C_2H_6	2	14	1	
C_2H_8	2	16	0	CH_4+CH_4
C_3H_2	3	14	5	Possible only in ring
C_3H_4	3	16	4	
C_3H_6.	3	18	3	
C_3H_8	3	20	2	
C_4H_2. .	4	18	7	
C_4H_4	4	20	6	 or as ring

of oxygen or argon. This suggests a very stable structure and Langmuir assumes accordingly that in the formation of a nitrogen molecule the ten electrons of the two kernels enter to form a *single octet* by pushing the two extra electrons (since there are ten electrons in the kernels of two nitrogen atoms) *inside the octet*, as shown in Fig. 7.

TABLE X

	n	e	p	Structural Formula
N_2O....	3	16	4	N=O=N or N=N=O
N_2O_2... ..	4	22	5	O=N−N=O
N_2O_3.....	5	28	6	O=N−O−N=O *or* O=N−N=O (O above N)
N_2O_4 ...	6	34	7	O=N−N=O (O above each N)
N_2O_5... ..	7	40	8	O=N−O−N=O (O above each N)

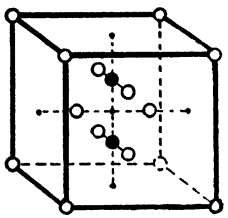


FIG. 7. Model of Nitrogen Molecule

"This structure of the nitrogen molecule," Langmuir writes, "explains in a perfectly satisfactory way all the remarkable properties of elementary nitrogen previously mentioned. The high heat of formation of nitrogen molecules from the atoms accounts for the great number of endothermic and explosive nitrogen compounds. It is also evident why elementary nitrogen is so unusually inert, while in its compounds it is one of the most active of the elements."

Carbon monoxide resembles nitrogen in most of its physical properties, such as freezing point, boiling point, critical pressure, viscosity, etc. The molecule of CO also contains ten electrons in the kernels of the two atoms. It therefore seems reasonable to conclude that the structures of the carbon monoxide and nitrogen molecules must be similar. In both molecules there is an imprisoned pair of electrons within the octet held as a stable pair by the two kernels.

Langmuir also suggests that the nitric oxide molecule (NO) probably has a structure similar to those of nitrogen and carbon monoxide. Since the molecule of NO contains one more electron than either of the two other molecules, it is assumed that the extra electron is held within the octet.

Finally, the fact that hydrocyanic acid (HCN) also has fourteen electrons (the same as in nitrogen and carbon monoxide) suggests that here again we have an octet with two electrons held inside. "The total charges on the kernels of nitrogen and carbon is 9 instead of 10 as in the nitrogen and carbon monoxide molecule. This somewhat decreases the stability and at the same time gives a negative charge to the CN radical so that it must combine with a hydrogen nucleus, or form a negative ion. Two such ions can combine by sharing a pair of electrons, thus releasing the electrons and leaving the uncharged cyanogen molecule $(CN)_2$. It is well known that cyanogen has a very close resemblance to chlorine in many ways. The theory of the con-

stitution given above indicates that this resemblance is not accidental, nor is it merely due to the fact that both ions are univalent. It depends on the fact that both the cyanogen ion and the chlorine ion have outside shells that consist of a single octet."

It is only fair to state that Lewis [1] disagrees with Langmuir's proposed structures for these four molecules and believes that the molecules should be represented as follows:

$$:N:::N:, \qquad :C:::O:(:C:::N:)$$

Valence, Coördination Number and Covalence: Langmuir distinguishes three different types of valence:

1. *Positive Valence:* the number of electrons an atom can give up.
2. *Negative Valence:* the number of electrons an atom can take up.
3. *Covalence:* the number of pairs of electrons which an atom can share with its neighbors.

Thus, lithium has a positive valence of one, while fluorine has a negative valence of one in most of its compounds. On the other hand, in F_2 it has a covalence of one. Carbon has a covalence of 4 in all its compounds, while the covalence of nitrogen may be 4, 3, or 2. The maximum covalence for nearly all the elements is 4, although, in certain exceptional cases which are discussed below, this rule is no longer valid.

In a large number of cases the covalence corresponds to Werner's coördination number, so that "the octet theory then corresponds exactly to Werner's theory just as for organic compounds it is equivalent to the ordinary valence theory." A number of illustrations of this correspondence will be found in Langmuir's original paper.

While the elements of the first short period never have a coördination number greater than 4, we find that in the second period silicon has a coördination number 6 in H_2SiF_6 and in a few other compounds. Similarly in PCl_5 and SF_6, phosphorus and sulphur apparently have coördination numbers greater than 4.[2]

This tendency to form compounds with a coördination number 6 is specially strong in the elements from titanium to nickel and the corresponding elements in the subsequent periods. Lewis has suggested [3] that in such cases "the electron pairs do not lie in the primary valence shell of the central atom, but in a secondary valence shell." Langmuir, on the other hand, assumes that in such a compound as H_2SiF_6, "the silicon atom does not share any pairs of electrons with the surrounding atoms but holds these by electrostatic forces." Thus the six fluorine atoms are located at the corners of an octahedron, forming an ion SiF_6^{--} which is capable of attaching to itself two hydrogen ions to form H_2SiF_6

[1] Valence, p. 127.

[2] See Lewis, Valence, pp. 101–2, for a discussion of these cases.

[3] Valence, p. 115.

Isosterism and Ismorphism: In the previous discussion, mention has been made that, on the basis of the octet theory, N_2O and CO_2 have similar structures. In both cases the molecule may be represented by three octets. Again, N_2, CO, NO and HCN are regarded by Langmuir as similarly constituted. Such molecules have been designated by Langmuir *isosteres* or isosteric compounds.[1] The term is, however, not restricted to chemical compounds but is also applicable to chemical radicals or to groups of atoms which hold pairs of electrons in common. The remarkable similarity in the physical properties of the isosteres of N_2 has already been discussed. Langmuir concludes that such similarities may be expected in all cases where we have groups of isosteres. The following table (Table XI) gives a list of isosteres of different types which may be expected on the basis of the octet theory:

TABLE XI

LIST OF ISOSTERES

Type	
1	H^-, He, Li^+
2	O^{--}, F^-, Ne, Na^+, Mg^{++}, Al^{+++}
3	S^{--}, Cl^-, A, K^+, Ca^{++}
4	Cu^+, Zn^{++}
5	Br^-, Kr, Rb^+, Sr^{++}
6	Ag^+, Cd^{++}
7	I^-, Xe, Cs^+, Ba^{++}
8	N_2, CO, CN^-
9	CH_4, NH_4^+
10	CO_2, N_2O, N_3^-, CNO
11	NO_3^-, CO_3^{--}
12	NO_2^-, O_3
13	HF, OH^-
14	ClO_4^-, SO_4^{--}, PO_4^{---}
15	ClO_3^-, SO_3^{--}, PO_3^{---}
16	SO_3, PO_3^-
17	$S_2O_6^{--}$, $P_2O_6^{----}$
18	$S_2O_7^{--}$, $P_2O_7^{----}$
19	SiH_4, PH_4^+
20	MnO_4^-, CrO_4^{--}
21	ScO_4^{--}, AsO_4^{---}

Langmuir points out that while the observed differences between the ordinary properties of the different isosteres of any one type are to be accounted for because of the differences in electric charge, "there is one property, namely, crystalline form, which should depend on the arrangement of the electrons in substances rather than upon the magnitude of the forces between their atoms. By a comparison of crystal form it should therefore be possible to obtain direct evidence of the similarity of the arrangement of the electrons in isosteric substances even if charges on the molecules are different."

Thus, since the ions O^{--}, F^-, Na^+ and Mg^{++} are isosteric, we would expect that MgF_2 and Na_2O should be isomorphous.

[1] *J. Am. Chem. Soc.*, **41**, 1543 (1919).

Since the nitrate and carbonate ions are isosteric, we should expect $NaNO_3$ and $MgCO_3$ to be isomorphous. As a matter of fact, this is actually found to be the case. A large number of other illustrations are discussed in detail by Langmuir. Table XII gives a list of typical cases of isomorphism based on isosterism and an examination of the crystallographic data shows that in all these cases the crystal structures are remarkably similar.

TABLE XII

TYPICAL CASES OF ISOMORPHISM BASED ON ISOSTERISM

Type Table XI	
2. .	(*a*) NaF–MgO; (*b*) MgF_2–Na_2O
3 .	(*a*) KCl–CaS; (*b*) $CaCl_2$–K_2S
5 . .	(*a*) RbBr–SrSe; (*c*) $SrBr_2$–Rb_2Se
7 .	(*a*) CsI–BaTe; (*c*) BaI_2–Cs_2Te
8.	N_2–CO
10	KNCO–KN_3, etc.
11	(*a*) $NaNO_3$–$CaCO_3$; (*b*) KNO_3–$SrCO_3$
14.	(*a*) $KClO_4$–$SrSO_4$; (*b*) $NaHSO_4$–$CaHPO_4$; (*c*) $KHSO_4$–$SrHPO_4$
15	(*a*) $NaClO_3$–$CaSO_3$; (*b*) $KHSO_3$–$SrHPO_3$
17	$Na_2S_2O_6$–$Ca_2P_2O_6$
18	$Na_2S_2O_7$–$Ca_2P_2O_7$
20	$RbMnO_4$–$BaCrO_4$
21	$MnSeO_4$ $2H_2O$–$FeAsO_4$ $2H_2O$

According to the ordinary valence theory, sulfur in sulfites and carbon in carbonates have the same valency, 4. It has, therefore, been concluded that these two classes of salts should be isomorphous. On the other hand, the same theory fails to predict the cases of isomorphism which do exist. The octet theory does not fail in either of these ways.[1]

While Langmuir has found his views to be strictly confirmed by the observations on isomorphous crystals, A. O. Rankine has shown that these views are in equally good agreement with molecular dimensions as derived from measurements of coefficients of viscosity of gases. Using the equations derived by S. Chapman [2] for the relation between coefficient of viscosity and molecular diameter, and combining these with the values for the atomic diameters of the rare gas molecules as derived by W. L. Bragg,[3] Rankine [4] concludes in agreement with Langmuir that "the molecules of CO_2 and N_2O behave not merely as though they had the same size and shape, but as if each of them had

[1] For a discussion of the further applications of the octet theory the reader is referred to the following papers: (1) Langmuir, *J. Am. Chem. Soc.*, **42**, 274 (1920), The Octet Theory of Valence and its Application with Special Reference to Organic Nitrogen Compounds; (2) E. C. Crocker, *J. Am. Chem. Soc.*, **44**, 1618 (1922), Applications of the Octet Theory to Single-Ring Aromatic Compounds; (3) Conant, *J. Am. Chem. Soc.*, **43**, 1705 (1921).

[2] *Phil. Trans.*, **216**, 279 (1916); also see Chapter III, Vol. I of this treatise and S. Dushman, High Vacuum, Chapter I, for a brief discussion of these relations.

[3] *Phil. Mag.*, **40**, 169 (1920).

[4] *Proc. Roy. Soc.*, **98**, 360, 369 (1920).

an external electron arrangement practically the same as that of three neon atoms in line and contiguous."

From measurements on the coefficients of viscosity of ammonia, phosphine and arsine, A. O. Rankine and C. J. Smith [1] conclude that in passing from neon to ammonia, argon to phosphine, and krypton to arsine the increases in mean diameter are approximately equal. This is to be expected since in each case three hydrogen nuclei have attached themselves to the atoms to complete the electron arrangement of the corresponding inert atom.

In a similar manner a most interesting confirmation of Langmuir's views on the isosteric nature of the nitrogen and carbon monoxide molecules has been obtained by C. J. Smith [2] from measurements of the coefficients of viscosity.

From X-ray measurements of the diameters of alkali and halogen ions, W. P. Davey [3] has also reached conclusions which are in accord with those predicted by Langmuir's theory with regard to similarity in atomic diameters of isosteres. Thus Cs^+, Xe, and I^-; Rb^+, Kr, and Br^-; K^+, Ar, and Cl^-, Na^+, Ne, and F^- are found to form groups such that in each of them the atomic diameter is constant. An interesting conclusion arrived at by Davey is that "the volume of the atom of the inert gas is roughly proportional to the number of electrons which it contains."

Generalized Theory of Valency: In a more recent paper which appeared in 1921,[4] Langmuir has shown that the rule of eight is essentially a special case of a much more general law. Before we can, however, proceed to state this law it is necessary to introduce two new terms.

Firstly, Langmuir designates the incomplete layer of electrons which constitute the valence shell (in contradistinction to the kernel) as the sheath. He defines this as follows: "The sheath of any atom (or atomic ion) consists of all the electrons in the outside layer *provided that this layer is incomplete* when the atom is electrically neutral. Thus atoms of the inert gases (neon, argon, etc.) and ions such as Na^+, Ca^{++}, etc., have *no sheaths* for the outside layers of these atoms consist of electrons which already form a complete layer in the neutral atom. The sodium *atom*, however, has an incomplete *sheath containing* one electron, while the fluorine atom has an incomplete sheath of 7 electrons. The fluorine *ion*, on the other hand, has a *complete sheath* of 8 electrons."

Assuming the arrangements assigned by Langmuir to the atoms of the inert gases, it requires 2, 8, 18, or 32 electrons to form a complete sheath, according to the period in which the atom belongs.

Now, as mentioned already, a given group of atoms may interact to complete their sheaths in two ways:

1. By *transfer of electrons* from one atom to another.
2. By *sharing one or more pairs of electrons.*

[1] *Phil. Mag.*, **42**, 601 (1921).
[2] *Proc. Phys. Soc.*, **34**, 155 (1922).
[3] *Phys. Rev.*, **22**, 211 (1923).
[4] *Science*, **54**, 59 (1921).

Such a pair of electrons is designated a *duplet.* If now we let e denote the number of electrons in the sheath of any neutral atom, let S denote the number of electrons in the sheath after the atom has interacted with others, and let P denote the number of duplets shared within the given group of atoms, then

$$\sum(e) = \sum(S) - 2P. \tag{3}$$

This is a more general statement of the relation given in equation (2). Furthermore, since positive valence differs from negative valence only in algebraic sign, Langmuir includes both under the term *electrovalence,* which is designated by the symbol v_e and is regarded as *positive when the atom gives up electrons.*

Hence, the electrovalence of any atom is given by the expression

$$v_e = e - S. \tag{4}$$

For electro-negative atoms, S is greater than e, so that v_e is negative.

If now we define the *covalence* (v_c) of an atom with neighboring atoms, we evidently have

$$\sum(v_c) = 2P. \tag{5}$$

For in adding up the values of v_c for all the atoms in a given group, we count each duplet (*bond*) twice.

From (3), (4) and (5) it follows that

$$\sum(v_e) + \sum(v_c) = 0. \tag{6}$$

That is, "*The sum of the electrovalences and covalences for all the atoms in any complete compound is zero.*

"If we represent $v_e + v_c$ by v, equation (6) takes the form

$$\sum v = 0 \tag{7}$$

for any complete compound, and this suggests that the quantity v may have some simple physical significance."

Now let us consider the application of these relations to different classes of chemical compounds.

1. *Complete Compounds:* These have completed sheaths, so that the number of electrons in the outside layer (in contradistinction to the kernel) is 0, 2, 18, or 32. "Since v_c in equation (6) can never be negative, v_e must be zero or negative. Therefore atoms having negative valences must always be present in a complete compound. Thus electro-positive elements do not form complete compounds with each other."

In compounds without covalence, equation (6) reduces to

$$\sum v_e = 0.$$

Therefore, such compounds must consist of positively and negatively charged ions. As typical of this class of compounds we have NaCl, and similar halides which are easily fusible and are good electrolytes; also such compounds as

$AlCl_3$, PCl_5, SF_6, etc., in which the electrovalency of Al is + 3, of P, + 5, and of S, + 6. Owing to the strong electrostatic forces between the positive and negative ions, the latter surround the former, producing only very *weak* external fields. These molecules are, therefore, quite stable and inert towards outside influences. Furthermore, owing to the strong internal forces, these latter compounds do not exhibit electrolytic conductivity, while the absence of strong external fields makes them quite volatile.

On the other hand, in the case of compounds without electro-positive atoms, we must find in accordance with equation (6) that the sum of the negative valences is equal to that of the covalences. Thus in CH_4, the covalence of carbon is 4, and the electrovalence of hydrogen is − 1. In H_2O, the covalence of oxygen is two, while in HF the covalence of fluorine is one.

Further consideration of such compounds leads, however, to a very important conclusion, which we may derive as follows:

If we denote negative valence by v_n, we can write equation (4) in the form

$$v_n = S - e. \tag{4a}$$

When one atom shares a duplet with another atom, we may regard the pair as divided equally between the two atoms. Hence, in accordance with equation (3), we will have *for each atom*

$$v_c = S - e.$$

It therefore follows that *for each atom* in such a compound

$$v_n = v_c$$

or

$$v = v_c - v_n = v_c + v_e = 0. \tag{8}$$

That is, the *covalence of each atom is equal to the negative valence of that atom.*

Let us now consider the magnitude of the charge on each atom in such a compound. Corresponding to v_n, the atom has a residual negative charge of v_n. But since the atom has a covalence v_c, and we have assumed that we may regard each pair of electrons as divided equally between the two atoms, the effective charge on the atom is $v_n - v_c = 0$.

Thus the *residual charge on each atom is zero.*

Langmuir sees in this conclusion a much more general relation which he states as a postulate in the following form:

"*The residual charge on each atom and on each group of atoms tends to a minimum.*"

Regarding the significance of this law he writes thus: "It is felt by the writer that this postulate is a crude expression of a very important and fundamental law. When we understand the repulsive forces between charged particles better, we shall be able to state the law in a more nearly quantitative form. The law is of very wide application. The uniformity of distribution of positive and negative ions in a salt solution is a familiar example of the

working of this law. In any small finite element of volume the charges of the positive and negative ions tend to be very nearly equal or the residual charge tends to a minimum.

"The preceding postulate expresses merely a *strong* tendency so that, in general, the charges of individual atoms are not necessarily zero. When the atomic charges depart from zero, however, they do so only as the result of a definite force or action which opposes the tendency of this postulate."

Such forces arise because of the strong tendency for the outside layers to assume the arrangement corresponding to a completed sheath. This would account for the existence of such highly positively charged ions as those in SF_6, etc.

As a further illustration of the application of these relationships let us consider the compound NH_4F. In NH_3, nitrogen has a covalency of 3 and its negative valency is also 3. When we form NH_4F, the fluorine atom tends to become negative at the expense of the nitrogen. "Thus the covalence of fluorine decreases to zero while that of nitrogen increases to four. The total number of covalence bonds has not been changed, they have merely been distributed differently. But this causes the atoms to become charged and makes the compound an electrolyte. It should be noted that this theory indicates definitely in what direction the change of charge occurs. Thus we should not expect NH_3 and HF to give a compound consisting of ions NH_2^- and H_2F^+ although under other conditions these ions might exist."

The main interest in this development of Langmuir's theory which has been sketched rather briefly in the preceding sections is that it presents an attempt to reduce valence conceptions in chemistry to a few laws which can be formulated algebraically. It represents one more stage in the gradual evolution of chemistry from a descriptive into an exact science of the same nature as physics. Although, up to the present, Langmuir has not developed his ideas any further, his ultimate ideal is best expressed by the concluding statement of his paper: "The writer plans to consider the quantitative aspects of these valence theories in subsequent papers. It is aimed to put the postulates (stated in the present paper) into a form that will permit at least rough calculations of the relative stabilities of various substances as measured, for example, by their heats of formation."

Bohr's Theory of Atomic Structure [1]

Spectral Series Relations: In discussing the derivation of the radiation laws, it was pointed out that all solid bodies emit a *continuous* spectrum when

[1] The literature on this subject is extensive. While references to detailed aspects are given in the corresponding sections, the following general reference works will be found extremely helpful: N. Bohr, The Theory of Spectra and Atomic Constitution, Cambridge Univ. Press, 1922; P. D. Foote and F. L. Mohler, The Origin of Spectra, The Chemical Catalog Co., 1922; A. Sommerfeld, Atomic Structure and Spectral Lines, Trans. from 3d German Edition by H. L. Brose, E. P. Dutton and Co., 1922; W. C. McC. Lewis, Quantum Theory, Longmans, Green and Co., 1919; N. R. Campbell, Modern Electrical Theory, Chapter XV, Series Spectra, Cambridge Univ. Press, 1921; *Naturwissenschaften*, 11, Heft 27 (1923).

in the incandescent state. In the case of gases and vapors, we observe that the spectrum is not continuous but consists either of sharply defined lines (*line-spectra*), or bands which extend over certain ranges of wave-lengths (*band-spectra*). The latter are characteristic of molecules, while the former are due to atoms. Both these types of spectra are observed in a Geissler tube containing hydrogen, the band spectrum being due to hydrogen molecules, while the line spectrum is due to atoms.

Now, while the band spectra form an extremely interesting topic and are becoming of interesting theoretical importance because of the information which they give us about the arrangement and relative distances between the atoms constituting the molecule, it is the line spectra which are of fundamental importance in the study of atomic structure. Since the time of Kirchhoff and Bunsen it has been recognized that each element possesses a characteristic line spectrum, and, as is well known, the applications of this fact in the field of spectroscopy have been extremely numerous and important.

The very existence of line spectra led physicists to conclude that the structure of the atom must be quite complex in order to give rise to such spectra. It was only, however, with the discovery of the existence of certain interesting relations among the lines of any one element that the foundations were laid for our present views on atomic structure. In 1885 Balmer pointed out that in the case of the ordinary spectrum of hydrogen there exists an interesting relation between the different lines. This spectrum (see Fig. 8) consists

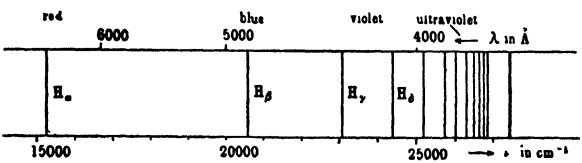


FIG. 8. Spectrum of Balmer Series

of a series of lines known as H_α, H_β, H_γ, H_δ, etc., extending from the red into the ultra-violet region. R. W. Wood [1] has been able to obtain photographs of this spectrum as far as the 20th line, while in photographs of nebular clusters the series have been obtained as far as the 33d line. Balmer observed that the wave-length of each of the lines of the series (then known) could be represented satisfactorily by the formula

$$\lambda = A \cdot \frac{n^2}{n^2 - 4}, \tag{1}$$

where λ denotes the wave-length, n has the values 3, 4, 5, 6, for H_α, H_β, H_γ, H_δ, respectively, and A is a constant.

The formula is more usually written in the form

$$\nu_0 = \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \tag{2a}$$

[1] *Proc. Roy. Soc.*, A 97, 455 (1920).

where $R = 109{,}677.69$, $n = 3, 4, 5, 6$, etc., and ν_0 is known as the *wave-number.*[1] This may also be written in the form

$$\nu = \frac{c}{\lambda} = Rc\left(\frac{1}{2^2} - \frac{1}{n^2}\right). \tag{2b}$$

It will be observed, especially from equation (2), that *Balmer's formula expresses the frequency as the difference between a constant term and a variable term.* Putting $n = \infty$, we obtain the *limiting frequency* or *head* of the series, corresponding to $\nu_0 = R/4$. This is represented in Fig. 8 by the line on the extreme right.

The next great discovery in regard to spectral series was made by Rydberg (1890) who showed that, for a number of elements (alkalis and alkaline earths), the lines could be arranged in definite series for each of which there exists a relation similar to Balmer's formula and involving the *same constant R* (known as Rydberg's constant).[2] Furthermore, it was shown by Rydberg and subsequently also by Ritz that different series for the same element are connected by a relation which is known as the *Principle of Combination.* The significance of this principle may be illustrated as follows: If in the case of hydrogen, we have the lines corresponding to

$$\nu' = Rc\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

and

$$\nu'' = Rc\left(\frac{1}{2^2} - \frac{1}{4^2}\right),$$

we ought to expect a line of frequency,

$$\nu''' = \nu'' - \nu' = Rc\left(\frac{1}{3^2} - \frac{1}{4^2}\right),$$

and a series of the general formula,

$$\nu = Rc\left(\frac{1}{3^2} - \frac{1}{n^2}\right). \tag{3}$$

Actually Paschen (1909) succeeded in finding such a series in the infra-red region of the hydrogen spectrum. Also Lyman (1904, 1906) observed a series in the ultra-violet regions corresponding to

$$\nu = Rc\left(\frac{1}{1^2} - \frac{1}{n^2}\right). \tag{4}$$

[1] The symbol ν_0 is used to differentiate it from $\nu = c/\lambda$, the frequency, where $c = 3 \times 10^{10}$ cm./sec.

[2] As a matter of fact, this "constant" is not exactly constant, but the differences for different elements are very small. The explanation for the existence of this variation in the cause of R was first given by Bohr in connection with his theory of the origin of spectra.

Quite recently F. S. Brackett[1] has discovered a series still further in the infra-red corresponding to

$$\nu = Rc\left(\frac{1}{4^2} - \frac{1}{n^2}\right). \tag{5}$$

Each of these series may be expressed by an equation of the type

$$\nu = Rc\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{6}$$

If we multiply each side by Planck's constant h, we obtain the relation

$$h\nu = Rch\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{7}$$

Since $h\nu$ corresponds, according to Planck's theory, to a quantum of energy of frequency ν, the inference is obvious that each of the terms on the right-hand side of equation (7) must also correspond to a quantity of energy, so that we may write

$$h\nu = E_n - E_m, \tag{8}$$

where E_n and E_m correspond to the energy of the system before and after *the emission* of the energy quantum $h\nu$. Furthermore, it follows that, apart from an additive arbitrary constant,

$$E_n = -\frac{Rch}{n^2}. \tag{9}$$

It is upon these considerations that Bohr has developed his theory of atomic structure.

Fundamental Assumptions of Bohr's Theory: Before proceeding to discuss this theory it is, however, necessary to renew briefly the essential features in Planck's radiation theory. In deriving the relation for the distribution of energy in a black-body enclosure, Planck introduced the conception of an oscillator vibrating with frequency ω. By studying the statistical equilibrium of a number of such oscillators in the field of radiation, Planck was led to the conclusion that the energy of any oscillator at any instant is equal to a whole multiple of an energy quantum which is proportional to the frequency ω. Thus the energy of the oscillator is given by the relation

$$E_n = nh\omega, \tag{10}$$

where n is a whole number.

According to classical theory, the frequency of the radiation (ν) emitted and absorbed by the oscillator is equal to its own frequency, that is, $\nu \equiv \omega$. Hence Planck's conclusion may be stated thus: An oscillator can emit and

[1] *Astrophys. J.*, **56**, 154 (1922)

absorb energy only in quanta of magnitude

$$\Delta E = h\nu, \tag{11}$$

where the *energy change is therefore determined by the frequency of the oscillator.*

In order to account for the existence of line spectra and their relationships as exhibited in equation (7), Bohr discards Planck's idea as expressed by equation (11) and assumes instead the relation expressed by equation (8). In other words, he assumes the relation

$$\nu = \Delta E/h. \tag{12}$$

That is, according to Bohr, the *frequency of the radiation is determined by the total energy change.*

"If this law is assumed," Bohr states,[1] "the spectra do not give us information about the motion of the particles in the atom as is supposed in the usual theory of radiation, but only a knowledge of the energy changes in the various processes which can occur in the atom. From this point of view the spectra show the existence of certain definite energy values corresponding to certain distinctive states of the atoms. These states will be called the *stationary states* of the atoms, since we shall assume that the atom can remain a finite time in each state, and can leave this state only by a process of transition to another stationary state."

Bohr's assumptions on which he bases his theory of spectral series have been stated by him in the following form.[2]

Postulate A. "An atomic system can, and can only, exist permanently in a certain series of states corresponding to a discontinuous series of values for its energy, and consequently any change of the energy of the system, including emission and absorption of electromagnetic radiation, must take place by a complete transition between two such states. These states will be denoted as the '*stationary states*' of the system."

Postulate B. That the radiation absorbed or emitted during a transition between two stationary states is monochromatic and possesses a frequency ν, given by the relation

$$h\nu = E_n - E_m. \tag{8}$$

As mentioned already, this leads to the conclusion that

$$E_n = -\frac{Rch}{n^2}, \tag{9}$$

where R is the Rydberg constant.

Derivation of Rydberg Constant: Now let us consider the application of these postulates to the simplest atomic system known, that of hydrogen, which consists of a nucleus of unit positive charge and an electron. According to Postulate A this system can exist in a series of stationary states, and while

[1] The Theory of Spectra, p. 23.

[2] On the Quantum Theory of Line Spectra (Copenhagen (1918)), part I, p. 5.

the transitions between these states are governed by Postulate B, it is assumed that in any stationary state the laws of ordinary (or Newtonian) mechanics may be applied.

In view of the existence of a force of attraction between electron and nucleus, it is necessary to postulate some balancing force, if the atom is to remain stable. The analogy between Coulomb's law of attraction and the force of gravity in celestial systems suggests that the electron in the hydrogen atom must describe a closed elliptical orbit with the nucleus at one of the foci. Under these conditions the force of attraction is balanced by the centrifugal force on the electron, and it is therefore assumed by Bohr that this is what occurs to make the stationary states of the hydrogen remain stable.

The same result may also be obtained by postulating the existence of a repulsive force as has actually been shown by Langmuir,[1] in which case the electrons must assume definite positions of equilibrium in the atomic structure. While this theory of a "static atom" might at first glance be considered as in much better agreement with the chemist's ideas of valency, it has, however, not been as fruitful a hypothesis as that of Bohr.

Let us now consider, from the point of view of Newtonian mechanics, an electron rotating about a nucleus of positive charge Ne in a circular orbit, where $N = 1$.

Let v = velocity of electron in orbit, $2a$ = diameter of orbit, ω = frequency of revolution. Then

$$v = 2\pi a\omega.$$

$$\text{Force of attraction} = \frac{e^2}{a^2}. \tag{10}$$

$$\text{Centrifugal force} = \frac{m'v^2}{a} = m'a(2\pi\omega)^2, \tag{11}$$

where m' = the mass of the electron.

Since the force of attraction must be equal to the centrifugal force, it follows from (10) and (11) that

$$\omega^2 = \frac{e^2}{4\pi^2 m' a^3}. \tag{12}$$

E, the total energy of the system, corresponds to the energy emitted as the electron approaches the nucleus. If we denote the total energy required to remove the electrons to infinity by W, it is evident that

$$W = -E. \tag{13}$$

Furthermore, the energy E is made up of the kinetic energy (E_k) and potential energy (E_p) of the electron in the orbit.

But

$$E_k = \tfrac{1}{2}m'(2\pi\omega a)^2 = \frac{e^2}{2a}. \tag{14}$$

[1] *Science*, **53**, 290 (1921).

"In this case the total energy of the atom is a minimum when the electron is in the inmost orbit, quantum number 1. When the electron is displaced to infinity, or just outside of the sphere of influence of the core, which practically is a very small distance, the total energy is all potential and is a maximum. Between these two positions we have many orbits where the electron assumes intermediate values of the total energy corresponding to the quantum numbers $n = 2, 3, 4$, etc. In general, it is more convenient to consider, instead of the total energy of the electron, the amount of work required to displace it from an inner to an outer orbit. Hence to the inmost orbit is ascribed the largest numerical value of the work, this being the work necessary to displace the electron to infinity. Such a diagram is shown in Fig. 10. The first orbit, $n = 1$,

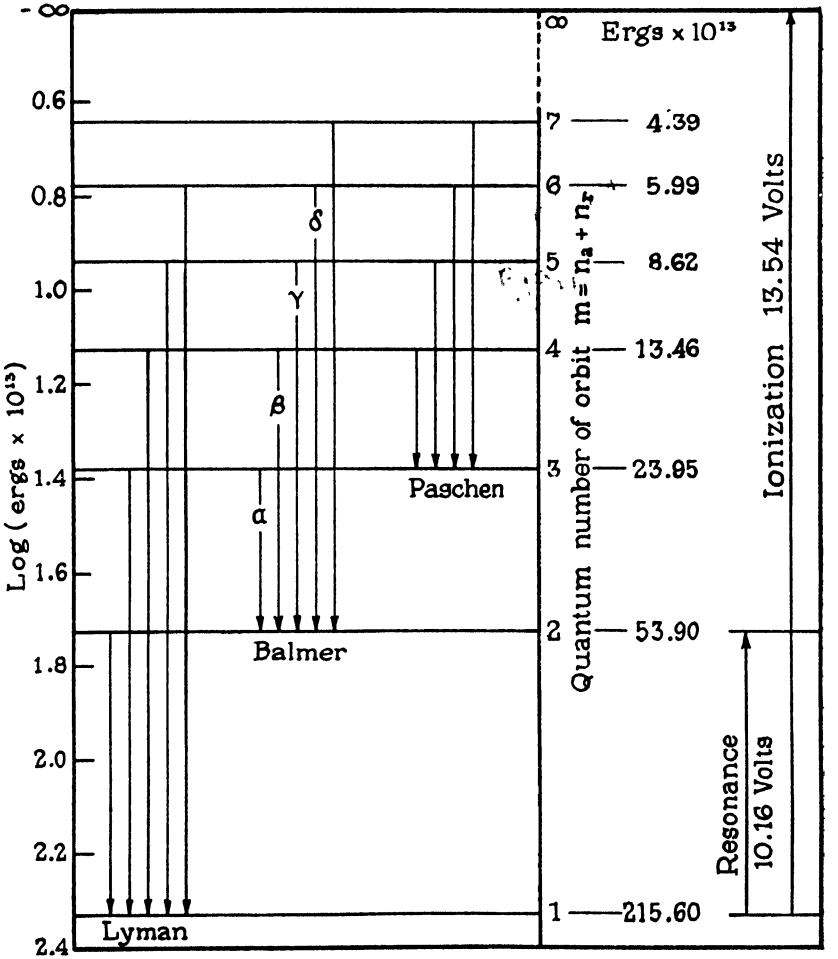


FIG. 10. Energy Diagram for Hydrogen

corresponds to 215.6×10^{-13} ergs;[1] the second to 53.9; the third to 23.95, etc. That is, it requires 215.6×10^{-13} ergs to completely remove the electron from its inmost stable position in the hydrogen atom, and 53.9×10^{-13} ergs to remove it from the second orbit, etc. The various series lines of hydrogen are shown in this diagram. For example, H_α represents a transition from orbit 3 to orbit 2. Referring to the energy scale on the right, we accordingly find that this represents an energy change of 3×10^{-12} ergs. (This value is obtained by taking the difference between the energy values corresponding to the head and tail of the arrow marked α. Note that *logarithms* of energy are plotted on the left in order to obtain an open scale.)"

Such energy diagrams may be constructed on the basis of the spectral series for a large number of atoms, and from these it is possible to calculate ionization and resonance potentials[2] in a similar manner to that employed in the case of the hydrogen atom.

Modification in the Theory for Atoms of Higher Atomic Number: If we assume that the nuclear charge, instead of being equal to $+ e$, is equal to $+ Ne$, we obtain the relations

$$a_n = \frac{n^2h^2}{4\pi^2m'e^2N}, \tag{29}$$

$$\omega_n = \frac{4\pi^2m'e^4N^2}{n^3h^3}, \tag{30}$$

and

$$\nu = RcN^2\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

$$= \frac{2\pi^2m'e^4N^2}{h^3}\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{31}$$

These equations may be applied to the case of ionized helium (He^+), corresponding to $N = 2$. The spectral series of this ion will be given by the general relation

$$\nu = 4\left(\frac{2\pi^2m'e^4}{h^3}\right)\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{32}$$

Accordingly, some of the lines of this series ought to correspond to those of the Balmer series for hydrogen and to a first approximation this is actually found to be the case.

A closer inspection shows, however, that there is a slight difference between the frequencies of lines in the two series, and it is one of the remarkable achievements of Bohr's theory that it enables us to calculate the exact magnitude of this difference.

[1] The values used by Foote and Mohler are based on slightly different values of the fundamental constants from those given above.

[2] See subsequent section for further discussion of ionization and resonance potentials.

In the preceding arguments the implicit assumption has been made that the mass of the nucleus is infinite as compared with that of the electron. Consequently we have considered only the motion of the electron about the nucleus. As a matter of fact, since the nucleus is not of infinite mass, both it and the electron *move in a circle about their common center of gravity.*[1] Therefore, the energy differences for the different stationary states are slightly different from those calculated previously. If we denote the nuclear mass by M, it is found that equation (23) must be replaced by the more exact relation

$$Rc = \frac{2\pi^2 m' e^4}{h^3\left(1 + \frac{m'}{M}\right)} = \frac{R_\infty c}{1 + \frac{m'}{M}}, \tag{33}$$

where R_∞ denotes the value derived in equation (23).

From the differences in wave-lengths of the He^+ lines and the H lines Paschen found the values

$$R_{He} = 109{,}722.144 \pm 0.04,$$
$$R_H = 109{,}677.691 \pm 0.06.$$

If we introduce these values into equations (23) and (33), it is found that they lead to the values

$$\frac{m_H}{m'} = 1847 \qquad \text{and} \qquad \frac{e}{m'} = 1.769 \times 10^7 \text{ e.m.u.}$$

These are in excellent agreement with values derived by other methods. Finally, from Paschen's values for R_H and R_{He} it follows that

$$R_\infty = 109{,}737.11 \pm 0.06.$$

Fine Structure of the Hydrogen Lines: We must now consider one other refinement of the previous calculations. If we compare the motion of the electron about the nucleus with that of a planet around the sun, we must also take into account the fact that *elliptic orbits are possible as well as circular orbits.* This possibility introduces a modification into the simple theory as outlined previously so that the energy corresponding to any given orbit of quantum number n is slightly different from that already calculated.

The essential conclusions obtained by this modified theory have been expressed most simply by Bohr as follows:[2]

"The calculation given above of the energy in the stationary states of the hydrogen system, where each state is characterized by a single quantum number, rests upon the assumption that the orbit of the electron in the atom is simply periodic. This is, however, only approximately true. It is found that if the change in the mass of the electron due to its velocity is taken into

[1] See Sommerfeld, Atomic Structure, and Foote and Mohler, Origin of Spectra, for further details on this point.

[2] Theory of Spectra and Atomic Constitution, pp. 67–8.

consideration the orbit of the electron no longer remains a simple ellipse, but its motion may be described as a central motion obtained by superposing a slow and uniform rotation upon a simple periodic motion in a very nearly elliptical orbit. For a central motion of this kind the stationary states are characterized by *two quantum numbers*. In the case under consideration one of these may be so chosen that to a very close approximation it will determine the energy of the atom in the same manner as the quantum number previously used determined the energy in the case of a simple elliptical orbit. This quantum number which will always be denoted by n will, therefore, be called the 'principal quantum number.' Besides this condition, which to a very close approximation determines the major axis in the rotating and almost elliptical orbit, a second condition will be imposed upon the stationary states of a central orbit, namely, that the angular momentum of the electron about the center shall be equal to a whole multiple of Planck's constant divided by 2π. The whole number, which occurs as a factor in this expression, may be regarded as the second quantum number and will be denoted by k. The latter condition fixes the eccentricity of the rotating orbit, which, in the case of a simple periodic orbit, was undetermined.

"The simplest description of the form of the rotating nearly elliptical electronic orbit in the hydrogen atom is obtained by considering the chord which passes through the focus and is perpendicular to the major axis, the so-called 'parameter.' The length $2p$ of this parameter is given to a very close approximation by an expression of exactly the same form as the expression for the major axis, except that k takes the place of n. Using the same notation as before, we have, therefore,

$$2a = n^2 \cdot \frac{h^2}{2\pi^2 N e^2 m'}, \qquad 2p = k^2 \cdot \frac{h^2}{2\pi^2 N e^2 m'} \cdot \tag{34}$$

For each of the stationary states which had previously been denoted by a given value of n, we obtain, therefore, a set of stationary states corresponding to values of k from 1 to n. Instead of the simple formula (22), Sommerfeld found a more complicated expression for the energy in the stationary states which depends on k as well as n. Taking the variation of the mass of the electron with velocity into account and neglecting terms of higher order of magnitude, he obtained

$$E_{n,\,k} = -\frac{2\pi^2 N^2 e^4 m'}{n^2 h^2}\left[1 + \alpha^2 N^2\left(-\frac{3}{4n^2} + \frac{1}{nk}\right)\right], \tag{35}$$

where $\alpha = \dfrac{2\pi e^2}{hc}$.

"Corresponding to each of the energy values for the stationary states of the hydrogen atom given by the simple formula (22), we obtain k values differing only very little from one another, since the second term within the bracket is very small. With the aid of the general frequency relation (8), we therefore obtain a number of components with nearly coincident frequencies instead of each hydrogen line given by the simple formula (26)."

The diagram shown in Fig. 11[1] represents an instantaneous aspect of the orbits of the different stationary states. The first number attached to each orbit gives the value of k, and the second that of $(n - b)$. Owing to the

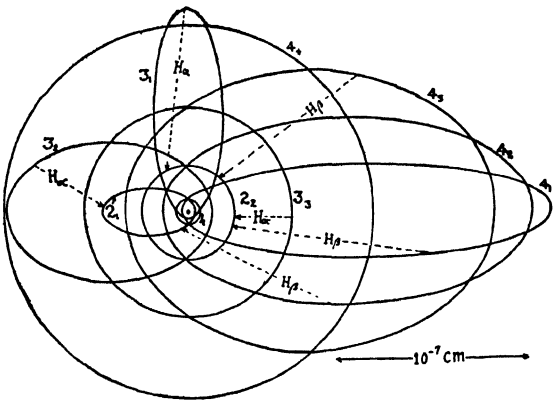


FIG. 11. Electron Orbits in Hydrogen Atom

relativity correction there is imposed on each of these orbits a slow rotation in its own plane about the nucleus as focus, and the resulting orbit, therefore, has the form of a rosette as shown in Fig. 12.

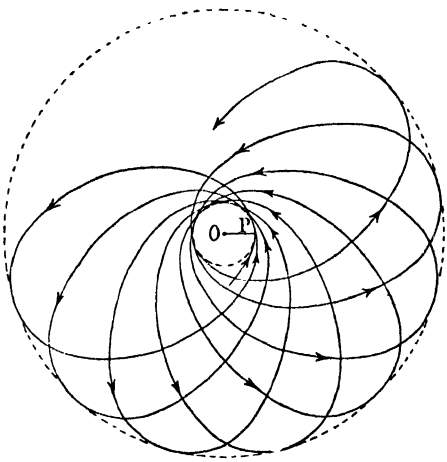


FIG. 12. Rosette

From Sommerfeld's formula it follows that each of the lines of the Balmer series should possess a fine structure corresponding to different values of k for constant values of n. Thus the line H_α is made up of three components which are indicated in Fig. 11 by dotted lines. These three lines may be regarded as a doublet one component of which has a satellite. For the frequency difference between the doublets Sommerfeld calculated the value

$$\Delta\nu_H = \frac{2\pi^2 e^4 m'}{h^3 n^4}\alpha^2 = 10^{10} \times 1.087, \tag{36}$$

since $n = 2$.

[1] Foote and Mohler, p. 22.

Expressed as wave-number, $\Delta\nu_H' = \frac{\Delta\nu_H}{c} = 0.365$ cm.$^{-1}$ Confirmation of this was obtained by Paschen from measurements on the spectrum of ionized helium for which according to the theory the separation should be four times as great. More recently, J. C. McLennan has obtained similar agreement in the case of the doublet separation for the lines of the Balmer series.[1]

Notation of Quantum Numbers: As stated in the previous section, Bohr distinguishes between the principal quantum number, n, and the subordinate quantum number k. In the literature on the Bohr theory it will be found that considerable reference is made to quantum numbers which have a somewhat different signification.[2] In the case of a circular orbit postulate A defines the orbit by the condition that the angular momentum of the electron must be equal to $nh/2\pi$, where n is the quantum number. When, however, we deal with an elliptical orbit, it is evident that the angular momentum is no longer constant for every point in the orbit. The velocity of the electron at any point in the orbit may be resolved into a component along the radius vector and another at right angles to this. It is therefore necessary to introduce two numbers, the *azimuthal* quantum number, n_a, corresponding to the latter motion and the *radial* quantum number, n_r, corresponding to motion along the radius vector.

It can readily be shown that Bohr's principal quantum number

$$n = n_a + n_r, \tag{37}$$

while the subordinate quantum number

$$k = n_a. \tag{38}$$

The eccentricity, ϵ, of the elliptical orbit is defined by the relation

$$1 - \epsilon^2 = \frac{n_a^2}{(n_a + n_r)^2} = \frac{k^2}{n^2}. \tag{39}$$

Also, the ratio of the minor axis, $2b$, to the major axis, $2a$, is given by the relation

$$\frac{b}{a} = \frac{k}{n} = \frac{n_a}{n_a + n_r}. \tag{40}$$

Significance of Quantum Numbers: The significance of the quantum numbers from the point of view of spectroscopy has been well summarized by McLennan as follows:[3]

"From the illustrations that have been given in the previous section, it will be seen that for a given atomic system the quantum numbers define the stationary states, and the energy values and moments of momentum of the

[1] *Brit. Ass. Rep.* (1923), Section A, Presidential address.

[2] For instance, Sommerfeld's Atomic Structure, also Foote and Mohler, Origin of Spectra.

[3] *Loc. cit.*

system in these states. Moreover, they define the kinematical character of the electron orbits in the atomic edifice, and on account of the simple relation connecting the values of spectral terms in the series spectrum of an element with the energy of the atom of this element in its various stationary states, they define these spectral terms and enable us to calculate their values.

"In the simplest possible treatment of a system such as that of the atom of hydrogen one quantum number n suffices to define the various factors just mentioned. In the theory of the fine structure of the spectral lines of hydrogen two quantum numbers n and k were required. In the case of a series spectrum of single lines two quantum numbers n and k are requisite to define its terms and the orbits corresponding to them. For a series spectrum consisting of doublets, triplets or multiplets, three quantum numbers are required, n, k, and j, to define its spectral terms and the corresponding electronic orbits. In the case of the resolution of a spectral line by the application of an external magnetic field a fourth quantum number m is necessary in order to distinguish the stationary states and to evaluate the spectral terms corresponding to the Zeeman components.

"Taking the case of the stationary states associated with the outer electrons in an atom for illustration, the kinematic significance of these quantum numbers is as follows: n characterizes the orbit forms of these outer electrons. If $n = k$, the orbit is circular, but if $n > k$, it is elliptical, having the greater eccentricity the greater n is compared with k. The quantum number k, on the other hand, connotes kinematically a rotation of the perihelion of the elliptical orbit confined in its own plane, and on account of this turning of the perihelion the orbit takes on the form of a rosette (as shown in Fig. 12). The normal to the orbital plane about which the perihelion is progressing is called the k axis. The quantum number j indicates the total moment of momentum of the atom. If an atom endowed with the motions described above be situated in an external magnetic field, the whole system thus in motion will carry out a rotation, i.e., a Larmor precession about the direction of the lines of force of this magnetic field. The axis for this rotation is called the m axis, and m is a measure of the moment of momentum about it.

"In spectroscopy it has become customary, in order to distinguish series of different kinds, to designate singlet systems by the use of capital letters, doublet series by Greek letters, and triplet series by small letters. Thus:[1]

$$\begin{aligned} \text{P S D F} &= \text{singlet systems,} \\ \pi\ \sigma\ \delta\ \phi &= \text{doublet systems,} \\ \text{p s d f} &= \text{triplet systems.} \end{aligned}$$

"In the same way it has become customary to use the same letters to designate the spectral terms whose differences determine the frequencies of the lines in a series. As examples we may cite 1S, 2S, &c.; 1π, 2π, &c.; 1d, 2d, &c.; and 1f, 2f, &c.

[1] A. Fowler, Report on Series in Line Spectra.

"Practically all efforts of spectroscopists towards arranging lines into series have had for their goal, even before the arrival of the quantum theory, in an unconscious way the establishment of the quantum numbers that define the various types of spectral terms indicated above. As a result of the progress that has been made in the last year or two, it is now generally agreed that the principal quantum number n determines the current number of the series term. For example, the 1S term is defined by $n = 1$, the 2P term by $n = 2$, the 3d term by $n = 3$, and the 4F term by $n = 4$, &c. The azimuthal quantum number k indicates the type to which a term belongs. For $k = 1$ an s, σ or S term is signified, for $k = 2$ a p, π or P term, for $k = 3$ a d, δ or D term, and for $k = 4$ an f, ϕ or F term. A 3_1 term, for example, would signify a 3s, a 3σ, or a 3S term, and a 4_2 term would be one which in spectroscopy is usually designated as a 4p, 4π or 4P term. We have then in the symbol n_k a means of defining a particular spectral term as well as a particular electronic orbit."

Arc and Spark Spectra: As a first approximation the frequency of the lines of many *arc spectra* can be represented by the Rydberg formula

$$\nu = Rc \left\{ \frac{1}{(n'' + \alpha_{k''})^2} - \frac{1}{(n' + \alpha_{k'})^2} \right\}, \tag{41}$$

where n'' and n' represent the principal quantum numbers and $\alpha_{k'}$ and $\alpha_{k''}$ are two constants for any series.

By means of this formula we obtain from an arc spectrum information about a series of states for which the energy of the atom in the nth state of the kth series is given by

$$E_{k(n)} = -\frac{Rch}{(n + \alpha_k)^2}. \tag{42}$$

This is very similar to the simple formula for the energy in the stationary states of the hydrogen atom.

"As regards the *spark spectra*, the structure of which has been cleared up mainly by Fowler's investigations, it has been possible in the case of many elements to express the frequencies approximately by means of a formula of exactly the same type as (41) only with the difference that the constant R, just as in the spectrum of ionized helium, is replaced by a constant which is *four times as large*. For the spark spectra, therefore, the energy values in the corresponding stationary states of the atom will be given by an expression of the same type as (42) only with the difference that R is placed by $4R$.

"This remarkable similarity between the structures of these types of spectra and the simple spectra given by hydrogen and ionized helium is explained simply by assuming the *arc spectra to be connected with the last stage in the formation of the neutral atom*, consisting in the capture and binding of the Nth electron. On the other hand, the *spark spectra are connected with the last stage but one in the formation of the atom*, namely, the binding of the $(N - 1)$th electron." [1]

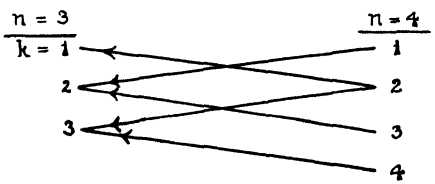
[1] N. Bohr, The Theory of Spectra, p. 77.

An extension of these conceptions has been furnished by the recent work of Paschen [1] and Fowler [2] on the spectra of doubly ionized aluminum and trebly ionized silicon. Paschen showed that under strong excitation aluminum emits a spectrum that can be arranged into series with a Rydberg constant equal to $9R$. Fowler has shown that in the spark spectrum of silicon there exists a series with a Rydberg constant of value $16R$. The spark spectrum of magnesium has been worked out by Foote and Mohler. We thus have a complete series beginning with neutral sodium, singly ionized magnesium (Mg^+), doubly ionized aluminum (Al^{++}) and trebly ionized silicon (Si^{+++}).

According to Bohr's theory, sodium is formed by adding one electron to the neon structure, magnesium by adding two, aluminum by adding three, and silicon by adding four. We would therefore expect the spectra of Na, Mg^+, Al^{++}, and Si^{+++} to be similar in type. This is confirmed by the observations on the spectra of these atoms. In a similar manner a series spectrum has been found in potassium which is similar to the arc spectrum of argon, and in general the *arc spectrum* of any element resembles the *spark spectrum* of the element of next higher atomic number.

These observations are in agreement with a general law of spectral series which is known as the *Kossel-Sommerfeld Displacement Law*, which will be referred to further in discussing X-ray spectra.

Selection Principle—Principle of Correspondence: Given two stationary states of the hydrogen atom for which the principal quantum numbers are n' and n'' and the subordinate quantum numbers k' and k'', the problem arises as to the possible transitions between these two states. We may also illustrate the problem more specifically thus: Suppose we have two stationary states whose principal quantum numbers are 3 and 4 respectively. What are the possible transitions? Since there are three orbits of quantum number 3 (corresponding to 3_1, 3_2, and 3_3) and four of quantum number 4, the first answer would be that there are 12 possible for which the subordinate quantum number increases or decreases by unity. Actually, only those are possible for which the subordinate quantum number changes by unity, and if we tabulate these cases we find that only 5 of these transitions may occur, as indicated by the arrows:



A Selection Principle was first derived by Rubinowicz [3] on the basis of the following considerations:

[1] *Ann. Physik*, **71**, 142, 537 (1923).

[2] *Proc. Roy. Soc.*, **103**, 722 (1923).

[3] *Ann. Physik*, **19**, 441, 465 (1918). See also S. Dushman, *J. Opt. Soc. Am.*, R. S. I., **6**, 235 (1922).

Rubinowicz argues that in the emission of radiation during the transition of an electron from one stationary state to another there must be equivalence, firstly, between the amount of energy emitted by the atomic system and that taken up by the ether as electromagnetic energy (this, of course, follows from the Law of Conservation of Energy), secondly, between the decrease in angular momentum of the electron and the increase in electromagnetic moment of momentum which can be ascribed to the spherical wave system produced in the ether. That is, Rubinowicz postulates the laws of conservation both with respect to energy and also electromagnetic momentum. Calculating the electromagnetic moment of momentum of the spherical wave by the method of classical electro-dynamics, he arrives at the conclusion that only those transitions between stationary orbits are possible for which the change in azimuthal quantum number (or first subordinate number, k) does not exceed unity. Thus if k_1 and k_2 denote the subordinate quantum numbers for two different orbits, there are three possibilities and only *three*, viz.:

$$\left.\begin{aligned} k_1 - k_2 &= \pm 1 \\ k_1 - k_2 &= 0 \end{aligned}\right\} \tag{43}$$

Furthermore, Rubinowicz finds that for $k = \pm 1$ the light emitted is circularly polarized. For the case $k = 0$, he concludes that the radiation is linearly polarized, or else there is no emission at all. As has been shown by Bohr, however, the case $k = 0$ is not possible.

Bohr has also deduced a selection principle which, while agreeing in the main with that derived by Rubinowicz, is more stringent, although derived from more general considerations. Bohr himself has designated this generalization as the *Principle of Correspondence*. In broad terms, the principle "gives expression," according to Bohr,[1] "to the tendency in the quantum theory to see not merely a set of formal rules for fixing the stationary states of atomic systems and the frequency of the radiation emitted by transitions between these states, but rather an attempt to obtain a rational generalization of the electromagnetic theory of radiation which exhibits the discontinuous character necessary to account for the essential stability of the atoms."

In deriving the value of the Rydberg constant in a previous section, use was made of the fundamental idea in Bohr's Correspondence Principle, which is that for the case where the quantum numbers n_1 and n_2 are very large compared to their difference,

$$\nu = \Delta n \cdot \omega, \tag{44}$$

where ω is the average frequency of rotation in the two orbits, and Δn obviously has an integral value.

Equation (44) is considered by Bohr to be of fundamental significance, as it shows that the frequency of radiation is an integral multiple, or *harmonic*, of the frequency of rotation. Now, in general, it is possible to resolve a rota-

[1] *Nature*, March 24, 1921, p. 194; also *Z. Physik*, **2**, 423 (1920); The Structure of the Atom, p. 81.

tion in an elliptical orbit into harmonics by the method of Fourier series. According to ordinary electrodynamic theory, these harmonics ought to appear in the radiation emitted, and the above deduction shows that for large values of n this conclusion is in agreement with the results derived on the basis of the quantum theory of spectral series. Thus we find an agreement for these extreme cases between the results to be expected on the basis of classical electrodynamics and those derived on the basis of the quantum theory. Of course, as pointed out by Bohr, there exists a signal difference in the mechanism of the radiation in the two cases. While according to electrodynamical theory all the harmonics ought to appear simultaneously, the quantum theory postulates that these harmonics appear as the results of transitions between different orbits not in the same atom and therefore independent of each other.

Now Bohr considers that this correspondence or coincidence in the values of the frequency of radiation as calculated from the two points of view cannot be accidental; the coincidence must also extend to amplitude and polarization of the light emitted. If we consider again the resolution of the frequency ν into harmonic components by the method of Fourier series, it is known that the coefficients in this series represent the amplitudes of the corresponding components and therefore their intensities. Hence, the intensity of the radiation corresponding to any particular frequency ν ought to be given by the corresponding coefficient in the Fourier series for the orbital frequency of the electron. This means that the *probability* of the existence of a certain value of ν in the frequency of the light emitted corresponds to the value of the coefficient of the corresponding harmonic component in the Fourier expansion. Thus *we obtain a criterion for determining the probability of a given transition between two stationary states.* If the harmonic corresponding to certain values of $n_2 - n_1$ is absent in the Fourier series for the rotational frequency of the electron, then it must be concluded that the transition corresponding to the difference $n_2 - n_1$ cannot occur, and the corresponding lines will therefore be absent in the spectrum.

This analogy must also extend to the polarization of the light emitted, since any single harmonic orbit must on the ordinary classical theory radiate circularly polarized light. Furthermore, Bohr holds that this analogy in polarization and intensity holds valid not only for low frequencies of orbital rotation, that is, low frequencies of radiation emitted, but also applies to higher frequencies.

We thus obtain a rule by which we can calculate the possible frequencies of radiation emitted in any given case by one or more electrons rotating in any orbits whatever round a nucleus. Firstly, we study the orbit from the point of view of ordinary electro-dynamics, and thus obtain a relation between orbital frequency of rotation of any electron and the various forces to which this electron is subjected. This orbital frequency is capable of resolution into harmonics, and from the nature of the coefficients it is possible to determine the relative intensities and polarization of the different frequencies that will appear as radiation. Since this calculation also gives the energy in any orbit

as a function of the rotational frequency, we then apply the quantum theory relation

$$h\nu = W_i - W_f$$

in order to calculate the corresponding spectral series.

Let us now consider from this point of view a simple hydrogen atom with an electron rotating in a circular orbit around a nucleus. If the diameters of the orbits corresponding to two stationary states are taken sufficiently large, we obtain the relation

$$\nu = (n_2 - n_1)\omega, \tag{44}$$

which connects the frequency of light emitted with the frequency of rotation. But for a circular orbit there is no possibility of any harmonic component, that is, $n_2 - n_1$ can only assume the values ± 1. The value $n_2 - n_1 = 0$ is obviously excluded. Thus we arrive at the Selection Principle derived by Rubinowicz for *azimuthal* quantum values of n.

Stark and Zeeman Effects: [1] A most interesting application of this Correspondence Principle has been made by Bohr in the determination of the effect on spectral lines of electrostatic and magnetic fields. The first of these is known as the Stark effect and the latter as the Zeeman effect.

In 1913 Stark discovered that the lines of the hydrogen spectrum are *split up into a number of polarized components* when radiating hydrogen atoms are exposed to strong electric fields (of the order of 100,000 volts per cm.). Subsequent investigations showed that similar phenomena occur in the case of a large number of other elements.

From the classical point of view the explanation of this effect is very difficult, but on the basis of Bohr's theory as modified by Sommerfeld through the introduction of elliptical orbits, a quantitative theory of the phenomenon was successfully worked out by K. Schwarzschild [2] and P. Epstein [3] in 1916.

Bohr has shown that the problem of the effect of electrostatic fields on radiating atoms may be dealt with rather simply on the basis of the Correspondence Principle. If we investigate by the methods of classical electrodynamics the effect of an electrostatic field on a simple elliptical orbit (such as that of hydrogen in state $n = 2$, $k = 1$), it is found that superposed upon the orbital frequency of rotation ω there is another frequency of perturbation σ given by the relation

$$\sigma = \frac{3eF}{8\pi^2 m' a\omega}. \tag{45}$$

In this relation, F denotes the strength of the field and the other symbols have the significance assigned previously.

[1] N. Bohr, The Effect of Electric and Magnetic Fields on Spectral Lines, *Phys. Soc.*, London, **35**, 275 (1923). L. Page, Dynamical Theories of Atomic Structure, *Nat. Res. Council Bulletin*, **2**, Part 6, 357 (1921).

[2] *Sitzber. preuss. Akad.*, April (1916).

[3] *Ann. physik*, **50**, 498 (1916).

We are therefore led to expect, from considerations similar to those which led to equation (44), that this frequency σ will appear as a series of harmonic components in the light emitted when the electron passes from one stationary state to another. Hence, the frequency of radiation emitted will be given for *small values* of both ω and σ by the approximate relation

$$\nu = (n_2 - n_1)\omega + (k_2 - k_1)\sigma, \tag{46}$$

where $n_2 - n_1$ is small compared to either n_2 or n_1 and the same statement holds true for k_2 and k_1. Furthermore, the intensities and state of polarization of the components corresponding to each line in the undisturbed state of the orbits can be derived by investigating the coefficients in the Fourier series expansion for the orbital frequency of rotation in the disturbed state. The results obtained in this manner are shown by Bohr to be in complete agreement with the actual observations.

It is evident that corresponding to any one stationary state of the undisturbed orbit there must be a number of stationary states in the disturbed condition. For the transition from one of these states to another, the change in energy E corresponding to one of these states in a powerful electrostatic field will be related to the energy E_n in the undisturbed state by the relation

$$E = E_n + kh\sigma. \tag{47}$$

This leads to the following relation for the frequency of the radiation emitted:

$$\nu = \frac{2\pi^2 e^4 m'}{h^3}\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\} + \frac{3hF}{8\pi^2 em'}\{n_2k_2 - n_1k_1\}. \tag{48}$$

The second term on the right-hand side corresponds to the difference between the frequency of the line in the normal spectrum and that produced in presence of an electrostatic field of strength F.

"In 1896 Zeeman discovered that the lines of the series spectra are influenced by magnetic means. In the simplest case there appear instead of one line, when viewed *longitudinally*, that is, when the ray is in the direction of the magnetic lines of force, two lines (*Zeeman doublet, longitudinal effect*), but when viewed *transversally*, that is, when the ray is perpendicular to the magnetic lines of force, instead of one line, three lines are observed (*Zeeman triplet, transverse effect*). Of the latter three lines one occupies the position of the original unresolved line, and the other two are displaced by equal amounts to greater or smaller wave-lengths, and occupy the same position in the spectrum as the two lines of the doublet in the longitudinal effect. The displacement amounts to

$$\Delta\nu = \frac{e}{m'} \cdot \frac{H}{4\pi c}, \tag{49}$$

where H = the intensity of the magnetic field." [1]

[1] A. Sommerfeld, Atomic Structure, 3d Edition, p. 294.

Bohr treats this phenomenon in exactly the same manner as the Stark effect. An investigation of the problem from the point of view of classical electro-dynamics leads to the conclusion that superposed upon the orbital rotation of the electron there is a uniform rotation of the entire system around an axis parallel to that of the field. The frequency of this rotation is given by the relation

$$\sigma = \frac{He}{4\pi m'c}. \tag{50}$$

This frequency must therefore appear as a harmonic in the spectral lines in accordance with equation (46), and corresponding to equation (48) for the Stark effect it is found that the change in frequency due to the magnetic field is given by equation (49).

A closer study of the effects to be observed shows that the only permissible values of $k_2 - k_1$ are ± 1 and 0. Thus, each line in the undisturbed states of the orbits exhibits three components in the magnetic field, one of which, the unaltered component, is linearly polarized parallel to the field, and the other two are circularly polarized in opposite directions when regarded along the direction of the field.

Ionizing and Radiating Potentials: In discussing Bohr's model of the hydrogen atom attention was drawn to the relation between the frequencies of lines in the spectral series and the values of the ionization and resonance potentials.

An excellent discussion of this subject has been given by A. Ll. Hughes,[1] and the reader is referred to this report for details as to the methods by which these potentials have been determined in different cases. The following explanation of the terms is taken from this summary.

"When a molecule is struck by a moving electron, the collision may, or may not, be an elastic one. By an elastic collision is meant one in which the electron rebounds with a negligible transfer of energy. (If the mass of the molecule were infinite compared with that of the electron, there would be no transfer of energy.) If there is a transfer of energy to a monatomic molecule, there may be complete ionization as shown by the production of positive and negative ions, or there may be 'partial ionization,' i.e., a disturbance of the atom, which is not detectable as ionization but is shown by the production of radiation. In the cases of polyatomic molecules, collisions are more or less inelastic, the transferred energy presumably being used up in increased motion of the component atoms relative to each other.

"The ionizing potential is the least potential through which an electron, starting from rest, must fall, to acquire sufficient kinetic energy to enable it to ionize a normal molecule on impact. Similarly a radiating potential measures the least kinetic energy which an electron must have, so that, on impact

[1] Report on Photo-Electricity including Ionizing and Radiating Potentials and Related Effects, *Bull. Nat. Res. Council*, **2**, Part 2, p. 84 (1921). See also C. B. Bazzoni, Ionization and Resonance Phenomena, *J. Franklin Inst.*, **196**, 627 (1923).

with a molecule, it may emit a monochromatic radiation characteristic of the molecule. (It is generally agreed that the radiation occurs afterwards as the molecule returns to its normal state.)"

In the simplest experimental arrangement the electrons emitted from a hot cathode are accelerated by applying positive voltages to a grid and the resulting positive ions are collected by a negatively charged plate situated behind the grid. It is observed that for any given gas no positive ions are produced until the electrons attain a certain critical voltage which we will designate by V_i. At potentials below this value it is, however, often observed that a photo-electric current is emitted by the collector plate when the accelerating potential exceeds a value V_r. This corresponds to the first resonance potential. Below this point the collision between electron and molecule is elastic.

The interpretation of these potentials in terms of Bohr's theory is very simple. When the atomic system absorbs energy corresponding to $V_r e$, one of the external (or valency) electrons is shifted from the normal state to a higher quantum state. The atom is then in a disturbed or *excited state* and on returning to the normal state energy is emitted in the form of a monochromatic radiation whose frequency must be governed in accordance with Bohr's second postulate by the relation

$$h\nu = V_r e. \tag{51}$$

Thus, the resonance potential corresponds to the first line in a spectral series of which the limiting frequency ν_∞ is given by a relation analogous to equation (52),

$$h\nu_\infty = V_i e. \tag{52}$$

These relations are of fundamental importance in connecting spectral frequencies with critical potentials. They may be expressed in ordinary units thus:

$$\left.\begin{aligned} \text{Energy} &= 1.59 \times 10^{-12} \text{ ergs} \\ V &= 4.118 \times 10^{-15}\, \nu \text{ volts} \\ \lambda &= 12{,}345/V \text{ Ångstroms} \end{aligned}\right\}. \tag{53}$$

The different stationary states of an atomic system and their energy relations may be represented by means of an energy diagram such as Fig. 10 in the case of hydrogen. For other atoms the diagrams are naturally more complex. Fig. 13 is a schematic representation of the different frequencies present in the arc spectrum of sodium.[1]

The normal orbit of the valency electron is that known as $1S$,[2] corresponding to the energy level

$$E = \frac{Rch}{(1+S)^2}, \qquad \text{or} \qquad \nu' = \frac{R}{(1+S)^2}, \tag{54}$$

where ν' is the wave-number.

[1] In this Figure ν (Foote and Mohler p. 53) represents the wave-number, that is, $1/\lambda$.

[2] The notation adopted in this discussion of spectroscopic data varies with different authors. In the present case we have used the notation given by A. Fowler, Report on Series

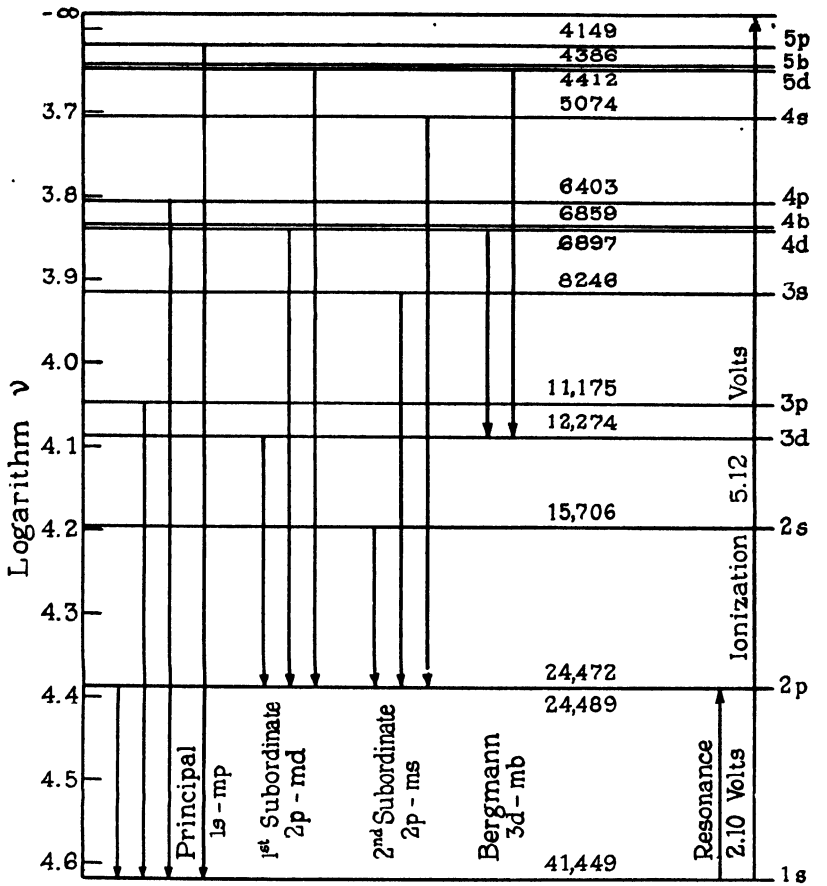


FIG. 13. Schematic Representation of the Arc Spectrum of Sodium

The lines of the *Principal Series* are produced by transitions from the mP levels, where $m = 1, 2, 3$, etc., to the 1S level. They are therefore denoted by the symbol $1S - m\mathrm{P}$. The first line of this series is given by the relation [1]

$$\nu_1' = R\left\{\frac{1}{(1+\mathrm{S})^2} - \frac{1}{(1+\mathrm{P})^2}\right\}, \qquad (55)$$

where ν_1' is the wave-number and $\nu_1' c$ is the corresponding frequency.

From equation (53) it follows that

$$V = \frac{12{,}345}{\lambda} = \frac{\nu'}{8102}.$$

in Line Spectra, *Phys. Soc.*, London, 1922. In the case of sodium the S series is really a doublet system and hence Fowler actually designates the terms as $m\sigma$, $m\pi$, etc.

[1] In the diagram the first level of the P series is denoted as 2P. According to Fowler's notation this should be 1P (or still more precisely 1π, since the P series consists of doublets).

Hence the ionization and resonance potentials should be given by the values

$$\left.\begin{aligned} V_i &= \frac{1S}{8102} = \frac{\nu_\infty'}{8102} \\ V_r &= \frac{1S - 1P}{8102} = \frac{\nu_1'}{8102} \end{aligned}\right\}. \qquad (56)$$

In the case of sodium, $\nu_\infty' = 41{,}449$. Hence $V_i = 5.12$ volts. Also $\nu_1' = 41{,}449 - 24{,}489 = 16{,}960$ for one line of the doublet and 16,977 for the other line. The corresponding value of V_r is 2.10 volts.

The mode of development of the other series is shown by the arrows which terminate in each case at the convergence frequency (corresponding to ν_∞' for the 1S level). It is obvious from equation (54) that for any one series the convergence frequency may be obtained from the series formula by placing the second term equal to zero. Such an energy diagram as Fig. 13 gives all mathematically possible series and combination lines which may be obtained by transitions from one level to any other. The only limitation to the possible transitions is, of course, the Selection Principle.

In order to indicate the quantum numbers for each stationary state (or energy level), Grotrian has developed a type of diagram such as shown in Fig. 14,[1] which represents the same series as the previous figure.

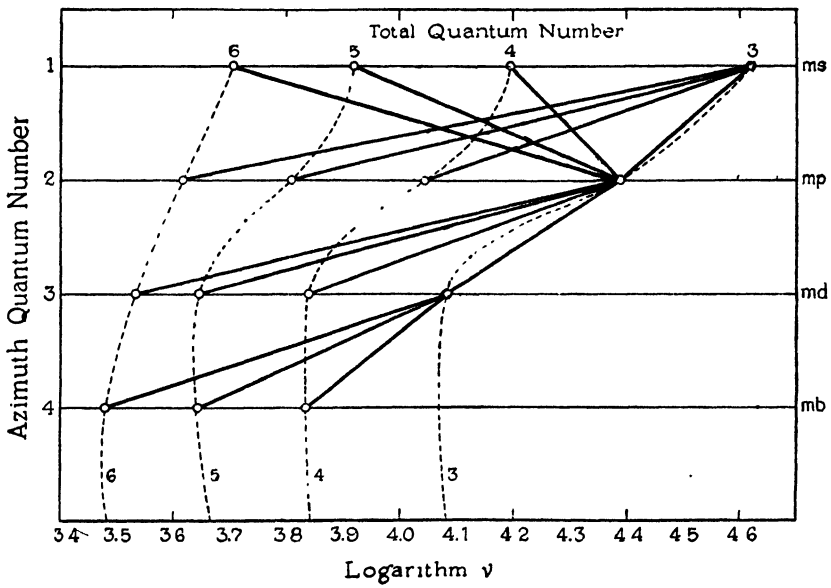


FIG. 14. Grotrian Diagram for Sodium Series

[1] Figs. 13 and 14 are taken from Foote and Mohler's The Origin of Spectra. The quotation in the text paragraph is from the same book, p. 59.

"Three coördinates are employed: as abscissa, logarithm of the wave-number; as ordinate, the azimuthal (Bohr's subordinate) quantum number, and a third system, indicated by dotted lines, the sum of azimuthal and radial quantum numbers (Bohr's principal quantum number). Each point shown by a small circle represents a wave-number or equivalent energy level. A spectral frequency is indicated by a straight line between two points and its numerical value is given by the difference in the wave-numbers corresponding to each end of this line. By the Bohr principle of selection the change in azimuthal quantum number = $\pm$ 1. Hence all straight lines representing spectral frequencies must terminate in adjacent horizontal lines of constant azimuthal quantum number." . . .

This identification of energy levels with spectral terms is the guiding principle of all the recent work on atomic structure. We must now proceed to present some of the experimental evidence which has served to confirm this point of view.

A large number of investigators (Foote and Mohler, McLennan, Davis and Goucher, Norton and Davies, Hughes, Franck and Hertz, K. T. Compton and others) have measured ionization and resonance potentials for a large number of vapors and gases.

Hughes has summarized these investigations as follows:

"The work of Franck and Hertz in 1914 must be regarded as the starting point of all work on radiating potentials, for they were the first to demonstrate that by bombarding the atoms of mercury vapor with electrons the single line λ 2536 appeared as soon as the energy of the electrons exceeded 4.9 volts. This was the first proof of the quantum relation as applied to the direct production of radiation by electron impacts, and, moreover, served to identify the radiation associated with the radiating potential as monochromatic light whose wave-length is that of the first line in an important series of the spectrum. McLennan and Henderson and McLennan extended this investigation to other metals. It was found that for Hg, Zn, Cd and Mg electrons must possess a certain characteristic minimum velocity before the single-lined spectrum of these elements could be called out, and that this minimum velocity agreed well with the value deduced by the quantum relation from the corresponding wave-lengths. These wave-lengths λ 2536 for Hg, λ 3076 for Zn, λ 3260 for Cd, and λ 2852 for Mg are all first lines of important series. The first three lines belong to the combination series, being $1S - 1p_2$, while the Mg line is the 1S $-$ 1P line. It should be noted here that Mohler and Foote in their experiments on radiating potentials found that the frequency $1S - 1p_2$ could be excited with Mg just as with the other elements. They state that their method really measures the points of inelastic impact hitherto taken to indicate the wave-length of the principal radiation. For Mg and Ca (and presumably Ba and Sr) the inelastic collision method emphasizes the frequencies $1S - 1p_2$ and indicates the presence of 1S $-$ 1P while the spectroscopic evidence emphasizes 1S $-$ 1P."

The following table taken from Hughes' report presents values of critical potentials for a number of metallic vapors as calculated from spectral terms

TABLE XIII

Metal	Series	Wave-length	Calculated Potential	
			Ionizing	Radiating
Mercury	1S	1187.96	10.392	—
	$1S - 1p_2$	2537.48	—	4.865
	1S − 1P	1849.60	—	6.674
Cadmium	1S	1378.69	8.954	—
	$1S - 1p_2$	3262.09	—	3.784
	1S − 1P	2288.79	—	5.394
Zinc	1S	1319.98	9.352	—
	$1S - 1p_2$	3076.88	—	4.012
	1S − 1P	2139.33	—	5.770
Magnesium	1S	1621.72	7.612	—
	$1S - 1p_2$	4572.65	—	2.700
	1S − 1P	2853.06	—	4.327
Barium	1S	2379.28	5.188	—
	$1S - 1p_2$	7913.52	—	1.560
	1S − 1P	5537.04	—	2.229
Strontium	1S	2176.94	5.671	—
	$1S - 1p_2$	6894.45	—	1.791
	1S − 1P	4608.61	—	2.679
Calcium	1S	2028.20	6.087	—
	$1S - 1p_2$	6574.59	—	1.878
	1S − 1P	4227.91	—	2.920
Cæsium	1σ	3191.37	3.873	—
	$1\sigma - 1\pi$	8523.33	—	1.447
		8945.82	—	1.378
Rubidium	1σ	2968.70	4.154	—
	$1\sigma - 1\pi$	7802.39	—	1.580
		7949.76	—	1.551
Potassium	1σ	2856.76	4.317	—
	$1\sigma - 1\pi$	7666.95	—	1.608
		7701.13	—	1.601
Sodium	1σ	2412.84	5.111	—
	$1\sigma - 1\pi$	5891.78	—	2.093
		5897.76	—	2.091
Lithium	1σ	2299.67	5.362	—
	$1\sigma - 1\pi$	6709.94	—	1.838
		6710.08	—	1.838

by means of the general relation $h\nu = Ve$. In all these cases agreement has been found between observed and calculated values.

While ionization and resonance potentials have been determined for a large number of gases (such as the rare gases, O_2, N_2, H_2, etc.), the relationship of these to spectral terms has not been so easy to unravel as in the case of metallic vapors. In this respect the determination of the energy levels in the helium atom has presented a very interesting problem. The spectrum of helium consists of two independent sets of series, principal, sharp, diffuse, and so on, exactly as if the gas were made up of two different atoms. In fact, at one time it was assumed that ordinary helium consists of two kinds of atoms, those of orthohelium and parhelium, the first being distinguished by a spectrum of doublets, the latter by one of single lines. The energy relations of these series are shown in Fig. 15[1] which represents the conclusions most generally accepted at the present time.

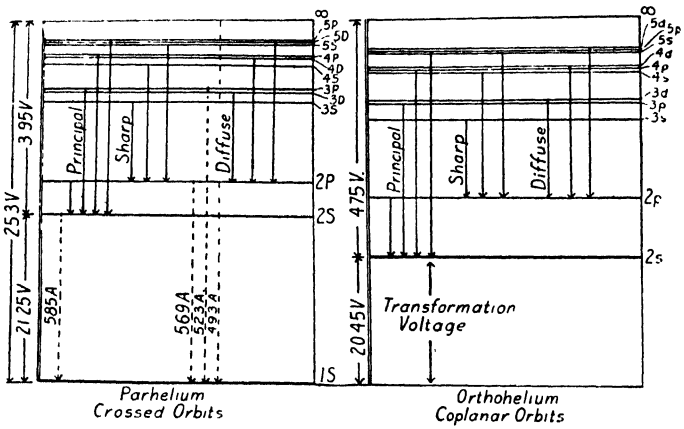


FIG. 15. Energy Levels in Helium

"The facts are these—that the normal atom is the 1S state of parhelium, that in this atom, called the crossed-orbit atom, the two electrons revolve in very slightly elliptical orbits inclined at an angle of 120 degrees to each other; that orthohelium is a metastable form, the lowest possible energy state being the 2s orbit which can be reached from the normal state only by an energy absorption from impact or ultra-violet radiation corresponding to 20.45 volts. This is called 'the transformation voltage.' In this metastable state the two electrons revolve in coplanar orbits one outside the other. For this reason orthohelium is frequently called 'coplanar' helium. This 2s state, possessing as it does considerable stability, serves as the fundamental orbit for the optical series of orthohelium. An energy absorption of 21.25 volts by the normal atom will give us parhelium in the 2S state which also possesses some stability

[1] Bazzoni, *J. Franklin Inst.*, **195**, 627 (1923). The quotation following this is taken from Bazzoni's paper.

though not as much as the 2s state, and is the fundamental orbit for the optical series of parhelium. The energy necessary to throw the electron into its 2s or 2S orbit, respectively 20.45 and 21.25 volts, plus that necessary to remove the electron from those orbits to infinity, respectively 4.75 and 3.95 volts, is taken to be the ionization energy of the normal atom. It will be seen that ionization is possible under this scheme with any electron bombardment energies greater than 20.45 volts but that true ionization by a single impact on a normal atom ought to require 25.3 volts."

A number of investigators have shown that helium has a resonance potential at 20.5 volts, another resonance potential at 21.3 volts and an ionization potential at 25.3 volts. "Of these potentials the first, 20.5 volts, is the transformation voltage which ought not to cause any radiation since the atom is thereby thrown into a metastable form from which it cannot return directly to the normal state. The second, 21.3 volts, corresponds to a radiation of wave-length 585 Å. and the third, the ionization potential 25.3 volts, to a radiation of wave-length 493 Å., which, therefore, ought to be the ultra-violet limit of the helium spectrum."

Recently G. Hertz [1] has measured the ionization and resonance potentials for neon and argon and obtained results which are in excellent agreement with spectroscopic data. The observations of Franck and Einsporn [2] on the various resonance potentials in mercury vapor should be mentioned in this connection. If we consider the energy diagram for any element, it is evident that corresponding to every energy level we ought to find a definite critical potential. Thus in the case of sodium, the first critical point occurs at 2.12 volts, corresponding to the transition 1S − 2P (see Fig. 13), but we should also find critical potentials corresponding to the transitions 1S − 3P, 1S − 4P, etc., 2P − 3d, etc. Actually Franck and Einsporn found in the case of mercury vapor 18 critical points between (and including) the first resonance potential at 4.68 volts and the ionization potential at 10.38 volts, some of these corresponding to definite spectral frequencies while others could not be interpreted in this manner.

Mention has been made previously of the observation by Franck and Hertz that by bombarding mercury atoms with electrons the single line λ 2536 appeared as soon as the energy of the electrons exceeded 4.9 volts. On the basis of Bohr's theory, we would expect that as the velocity of the electrons is increased beyond this point other lines should appear until finally the whole spectrum appears when the potential reaches the ionizing value. While previous attempts to confirm this conclusion led to negative results, J. A. Eldridge [3] has very recently obtained such confirmation in the case of mercury vapor by adopting a somewhat different technique to that used by other investigators.

Line Absorption Spectra. Resonance Radiation and Excited Atoms: In order to bring an atom into a condition in which radiation is emitted, it is

[1] *Z. Physik*, **18** (1923).

[2] *Z. Physik*, **2**, 18 (1920). See also Foote and Mohler's Origin of Spectra, p. 137.

[3] *Phys. Rev.*, **23**, 685 (1924); see also Hertz, *Z. Physik*, **22**, 18 (1924).

necessary to eject an electron from its normal orbit to an outer orbit of higher quantum number and therefore of higher energy content. An atom in this condition is said to be in the *excited state*, and the properties of such atoms have recently received a great deal of attention from a number of investigators.[1]

It is evident that in order to produce such excited atoms the normal atoms must be subjected either to (1) electrons having a velocity which is not less than the first resonance potential or (2) radiation whose frequency corresponds to the first resonance potential. (There are other methods but we shall not discuss these in the present connection.) In either case the energy $Ve = h\nu$ is communicated to the atom. The absorbed energy is re-emitted with the same frequency and we thus have the phenomenon of *resonance radiation*. Thus R. W. Wood and Dunoyer[2] showed that sodium light passed through sodium vapor caused the emission of the D lines. More recently Füchtbauer[3] has shown that mercury vapor stimulated by radiation of wave-length λ 2536 emits a spectrum in which there are over thirty lines whose frequencies can be measured. In this case the absorbed radiation produces excited atoms in the $2p_2$ state. By further absorption of radiation, these are raised to the 3D state. As these excited atoms return to their normal state, radiations of different frequencies are emitted and a spectrum is obtained.

The most important observation in this connection is that the unexcited atom absorbs only that frequency of radiation which corresponds to a possible transition from the zero level to some higher level in the energy diagram of the atom.

By further absorption of energy, or by electron impact, an atom in the excited state may be raised to a still higher energy level. This accounts for the production of arcs in gases at voltages below the ionizing potential.[4] The process of ionization by electron impacts in successive stages is known as *cumulative ionization*. This phenomenon and that of energy transfer by radiation depend upon the fact that while the life of an excited atom is small it is yet of measurable duration. W. Wien has shown that the value of τ, the average life, is 2.3×10^{-8} sec. for certain states of the hydrogen atom, while recent calculations by R. C. Tolman[5] lead to the conclusion that for mercury emitting the line λ 2536, $\tau = 1.03 \times 10^{-7}$ sec., and for iodine emitting λ 5461, $\tau = 3 \times 10^{-3}$ sec.

Klein and Rosseland[6] have pointed out that while electrons may transfer their kinetic energy to normal atoms and thus put them into the excited state, it is also to be expected that collisions exist which involve exactly the reverse type of energy transfer. In such collisions (known as those of the *second kind*

[1] K. T. Compton, Properties of Excited Atoms, *J. Opt. Soc. Am.* and *R. S. Inst.*, **7**, 955 (1923). This paper presents an excellent summary of a large number of investigations on this subject.

[2] *Phil. Mag.*, **27**, 1018 (1914).

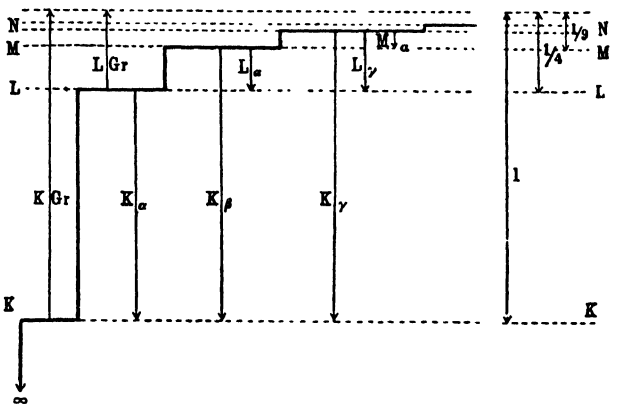
[3] *Z. Physik*, **21**, 635 (1920).

[4] See numerous papers by K. T. Compton and his students in *Physical Review*, 1920–1924.

[5] *Phys. Rev*, **23**, 693 (1924).

[6] *Z. Physik*, **4**, 46 (1921).

is to be considered at $-\infty$. The highest dotted limit of the steps corresponds to the periphery of the atom. The quantitative drawing of the picture leads us to assign to the successive steps K, L, M, N, ··· the series of integral



FIGS. 16 AND 17. Process of Excitation

'quantum numbers' 1, 2, 3, 4, ··· in such a way that the position of each step below the highest level is, at least to a certain degree of approximation, proportional to

$$\frac{1}{1^2}, \frac{1}{2^2}, \frac{1}{3^2}, \frac{1}{4^2}, \cdots.$$

Accordingly we make the height of the steps in the figure decrease, from the bottom upwards, in the manner indicated by the differences of height 1, $\frac{1}{4}$, $\frac{1}{9}$, ··· written at the side (on the right). Moreover, we again draw the arrows K_α, K_β, ··· L_α ··· that correspond to the various possibilities of energy-emission, and the arrows K–Gr, L–Gr, which correspond to the various kinds of energy absorption."

The frequencies ν_K, ν_L, etc., which correspond to the limits of the K-, L_1-series, etc. (in the same manner as the series limits for visible spectra), have an important physical significance. If we wish to obtain say the line K–α (the lowest frequency of the K-series) from a given anticathode material and apply the voltage given by the quantum relation

$$V_\alpha = \frac{h\nu_\alpha}{e},$$

we do *not* obtain the desired line. Rather we must increase the voltage on the X-ray tube to the value V_K (corresponding to ν_K) at which all the lines of the K-series then appear simultaneously.[1] The obvious explanation is that

[1] D. L. Webster, *Phys. Rev.*, 7, 599 (1916); *Proc. Nat. Acad. Sci.*, 2, 90 (1916). See also L. Page (*loc. cit.*).

in order to obtain any K-radiation at all an electron must be removed from the K-shell and then electrons can move into this shell from the outer shells.

Similarly, to excite any line of the L-series it is necessary to apply a voltage greater than that corresponding to ν_L. As a matter of fact there are three L-levels and the same statement holds true for each level, so that by carefully regulating the voltage we can produce rays of the L_1-series but not those of the L_2-series ($\nu_{L_2} > \nu_{L_1}$). Thus, in the case of tungsten the three excitation limits are:

L_1-limit,	$V = 10.2$	kilovolts.
L_2- "	$V = 11.6$	"
L_3- "	$V = 12.0$	"

The phenomena observed in the absorption of X-rays are also accounted for in the same manner. As was mentioned in the discussion of resonance potentials, absorption of a given frequency in the visible region by an atom occurs if the energy $h\nu$ corresponding to this frequency is equal to the energy required to shift an outer electron from the normal orbit to the next one further out. It is evident that in the case of X-rays the energy absorbed must be sufficient to remove an electron from one of the inner shells to the periphery of the atom. "Thus the *excitation limits become marked in the continuous X-ray absorption as absorption limits.* For frequencies below the limiting frequency, for, say, K-radiation from a given material, the absorption is weak. But, at the limiting frequency, the selective absorption of the material comes into play and this absorption then persists for higher frequencies.

"These observations are all in agreement with the view that in the normal atom the electrons are distributed in shells and that absorption cannot occur until sufficient energy has been supplied by the incident radiation to remove an electron from one of these shells to the periphery of the atom.

"There is one deduction which follows from these considerations and which was derived by Kossel. Let ν_K be the absorption frequency corresponding to the removal of an electron from the K-ring to the surface of the atom, and ν_L the corresponding quantity for the L-ring. Then, assuming the second postulate of the Bohr theory to apply to absorption as well as to emission, we should have

$$\nu_L + \nu_{K_\alpha} - \nu_K = 0$$

(where ν_{K_α} is the frequency of the K_α line), a relation which has been well confirmed by experiment." [1]

It will be recognized that Kossel's relation is analogous to the Ritz combination principle for visible spectra [2] and in the classification of X-ray spectra this principle has been found invaluable.

Since the absorption limits correspond to energy levels, it is obvious that, from the observation of these, it is possible to determine quantitatively the

[1] L. Page, *loc. cit.*, p. 381.

[2] D. Coster, "On the Combination Principle in the Röntgen Series," *Z. Physik.*, **5**, 139 (1921); **6**, 185 (1921).

various energy levels in any atom. From the values of these energy levels, certain conclusions may be drawn regarding the quantum numbers of the orbits. Thus, from equation (57) which represents Moseley's law, we have, for the energy level of the K-shell, the value

$$h\nu_{\mathrm{K}} = W_{\mathrm{K}} = -Rch(N-1)^2\left(\frac{1}{1^2}\right). \tag{58}$$

and for that in the L-shell, the value

$$h\nu_{\mathrm{L}} = W_{\mathrm{L}} = -Rch(N-1)^2\left(\frac{1}{2^2}\right). \tag{59}$$

In each case $\sqrt{\frac{\nu}{Rc}} = \frac{(N-1)}{n}$, where n is the quantum number of the orbit. If, for the same characteristic line, we plot $\sqrt{\frac{\nu}{Rc}}$ against $N-1$, we obtain, as a first approximation, a straight line whose slope is $\frac{1}{n}$, that is, the *reciprocal of the quantum number* corresponding to the particular level. In this manner we obtain, for the K-shell, $n = 1$, for the L-shells, $n = 2$, and so forth.

However, this presents the results actually obtained only crudely. There is an apparent arbitrariness in Moseley's relation in the use of $N-1$ instead of N, and in general it has been found necessary, in order to obtain agreement with a relation of the type of equation (58) or (59), to replace N, the real atomic number, by $N-\gamma$, the so-called *effective nuclear charge*.

The situation is complicated still more by the necessity of introducing subordinate quantum numbers k_1 and k_2.[1] That is, it is necessary to consider the existence of elliptic as well as circular orbits. This in turn leads, as in the case of the elliptic hydrogen orbits, to a *fine structure of X-ray lines*.

It is of interest to point out in this connection that, as has been shown by Sommerfeld, the separation of the lines in the X-ray region, owing to the relativity correction, is very large compared with that observed in the case of hydrogen and ionized helium. Referring to equation (35) it will be observed that $\Delta\nu$ varies as N^4. This means that, for uranium ($N = 92$), the separation of the doublets is seventy million times as great as for hydrogen. This has been confirmed by direct observation on doublets in the L- and M-series.

Spatial Arrangement of Orbits in Atoms: In consequence of these observations on X-ray spectra Bohr concludes that the atomic model which has been discussed so far cannot be adequate. Rather it is necessary to ascribe *a definite orbit to each electron in the atom*. These orbits are represented to a first approximation by the symbol n_k, where n denotes the principal quantum number and k the subordinate quantum number. For k small compared with

[1] These are the designations used by N. Bohr and D. Coster, *Z. Physik.*, **12**, 342 (1923). This is an extremely comprehensive paper on the classification of X-ray spectra and the relation of these to the periodic system of the elements. See also papers by Bohr and Coster in *Naturwissenschaften*, **11**, 567, 606 (1923).

n the orbit is very eccentric and the electron thus approaches the nucleus very closely at its minimum distance (perihelion position). Furthermore, the orbits of the different electrons are assumed to be arranged spatially, that is, in three dimensions. It is readily seen that by arranging the orbits in certain relative positions to each other, Bohr has attained virtually the same result as Langmuir and Lewis in their theory of the static atom.

The manner in which Bohr has developed his most recent conceptions on atomic structure is best described in his own words in the following paragraphs:[1]

"We attack the problem of atomic constitution by asking the question: 'How may an atom be formed by the successive capture and binding of the electrons one by one in the field of force surrounding the nucleus?'

"Before attempting to answer this question it will first be necessary to consider in more detail what the quantum theory teaches us about the general character of the binding process. We have already seen how the hydrogen spectrum gives us definite information about the course of this process of binding the electron by the nucleus. In considering the formation of the atoms of other elements we have, also, in their spectra, sources for the elucidation of the formation processes, but the direct information obtained in this way is not so complete as in the case of the hydrogen atom. For an element of atomic number N the process of formation may be regarded as occurring in N stages, corresponding with the successive binding of N electrons in the field of the nucleus. A spectrum must be assumed to correspond to each of these binding processes; but only for the first two elements, hydrogen and helium, do we possess a detailed knowledge of these spectra. For other elements of higher atomic number, where several spectra will be connected with the formation of the atom, we are at present acquainted with only two types, called the 'arc' and 'spark' spectra respectively, according to the experimental conditions of excitation. Although these spectra show a much more complicated structure than the hydrogen spectrum, given by formula (26) and the helium spectrum given by formula (32), nevertheless in many cases it has been possible to find simple laws for the frequencies, exhibiting a close analogy with the laws expressed by these formulæ."

Bohr then discusses the relation between arc and spark spectra. As shown in a previous section (see page 1096), the two types of spectra can be expressed by means of formulæ of the same type, the only difference being that the Rydberg constant (R) which is observed in the case of arc spectra has to be replaced by $4R$ in the case of spark spectra.

"This remarkable similarity," Bohr states, "is explained simply by assuming the arc spectra to be connected with the *last stage in the formation of the neutral atom* consisting in the capture and binding of the Nth electron. On the other hand, the spark spectra are connected with the *last stage but one in the formation of the atom*, namely, the binding of the $(N - 1)$th electron. In these cases the field of force in which the electron moves will be much the same as that surrounding the nucleus of a hydrogen or helium nucleus respectively,

[1] N. Bohr, The Theory of Spectra and Atomic Constitution, p. 75 *et seq.*

at least in the earlier stages of the binding process, where during the greater part of its revolution it moves at a distance from the nucleus which is large in proportion to the dimensions of the orbits of the electrons previously bound."

Unfortunately our knowledge of spark spectra and spectra of still higher orders (involving $9R$ and $16R$) is still quite meagre. "For this reason there exist wide gaps in the experimental evidence for the successive capture of electrons, especially in a heavy element, which must be bridged by assumptions in regard to what the spectrum should be were it known, and by comparison with the stages in the building of atoms where the spectral data are more complete. These difficulties are quite serious in the determination of the outer structure of an atom, in fixing the type of orbits occupied by the loosely bound electrons which are effective in chemical reactions." [1]

The case is, however, different when we consider X-ray spectra. As Bohr has expressed it, "While the characteristic change of the chemical properties with atomic number is due to the gradual development and completion of the groups of the loosest bound electrons, the characteristic absence of almost every trace of a periodic change in the X-ray spectra is due to two causes. Firstly, the electronic configuration of the completed groups is repeated unchanged for increasing atomic number, and secondly, the gradual way in which the incomplete groups are developed implies that a type of orbit, from the moment when it for the first time appears in the normal state of the neutral atom, always will occur in this state and will correspond to a steadily increasing firmness of binding. The development of the groups in the atom with increasing atomic number, which governs the chemical properties of the elements, shows itself in the X-ray spectra mainly in the appearance of new lines. We can only expect a closer connection between the X-ray phenomena and the chemical properties of the elements when the conditions on the surface of the atom are concerned. In agreement with what has been brought to light by investigations on absorption of X-rays in elements of lower atomic number, such as have been performed in recent years in the physical laboratory at Lund, we understand immediately that the position and eventual structure of the absorption edges will to a certain degree depend upon the physical and chemical conditions under which the element investigated exists, while such a dependence does not appear in the characteristic emission lines.

"If we attempt to obtain a more detailed explanation of the experimental observations, we meet the question of the influence of the presence of the other electrons in the atom upon the firmness of the binding of an electron in a given type of orbit. This influence will, as we at once see, be least for the inner parts of the atom, where for each electron the attraction of the nucleus is large in proportion to the repulsion of the other electrons. It should also be recalled that, while the relative influence of the presence of the other electrons upon the firmness of the binding will decrease with increasing charge of the nucleus, the effect of the variation in the mass of the electron with the velocity upon the firmness of the binding will increase strongly. This may

[1] P. D. Foote, Address at Am. Inst. Chem. Eng., Dec. 1923.

be seen from Sommerfeld's formula (35). While we obtain a fairly good agreement for the levels corresponding to the removal of one of the innermost electrons in the atom by using the simple formula (35), it is, however, already necessary to take the influence of the other electrons into consideration in making an approximate calculation of the levels corresponding to a removal of an electron from one of the outer groups in the atom. Just this circumstance offers us, however, a possibility of obtaining information about the configurations of the electrons in the interior of the atoms from the X-ray spectra. Numerous investigations have been directed at this question both by Sommerfeld and his pupils and by Debye, Vegard and others. It may also be remarked that de Broglie and Dauvillier in a recent paper have thought it possible to find support in the experimental material for certain assumptions about the numbers of electrons in the groups of the atom to which Dauvillier had been led by considerations about the periodic system similar to those proposed by Langmuir and Ladenburg. In calculations made in connection with these investigations it is assumed that the electrons in the various groups move in separate concentric regions of the atom, so that the effect of the presence of the electrons in inner groups upon the motion of the electrons in outer groups as a first approximation may be expected to consist in a simple screening of the nucleus. On our view, however, the conditions are essentially different, since, for the calculation of the firmness of the binding of the electrons, it is necessary to take into consideration that the electrons in the more lightly bound groups in general during a fraction of their revolution will penetrate into the region of the orbits of electrons in the more firmly bound groups. On account of this fact, many examples of which we saw in the series spectra, we cannot expect to give an account of the firmness of the binding of the separate electrons, simply by means of a 'screening correction' consisting in the subtraction of a constant quantity from the value for N in such formulæ as (31) and (35). Furthermore, in the calculation of the work corresponding to the energy levels, we must take account not only of the interaction between the electrons in the normal state of the atom but also of the changes in the configuration and interaction of the remaining electrons, which establish themselves automatically without emission of radiation during the removal of the electron. Even though such calculations have not yet been made very accurately, a preliminary investigation has already shown that it is possible approximately to account for the experimental results."

The X-ray spectra may therefore be considered as indicating the process by which an atom undergoes reorganization after a disturbance in its interior. It has been shown that the energy necessary completely to remove an electron of quantum designation n_k from an atom of nuclear charge N is given by a general relation of the form

$$W = Rch\left[\frac{(N-\gamma)^2}{n^2} + \frac{(N-\delta)^4}{n^4}\left(\frac{2\pi e^2}{hc}\right)^2\left(\frac{n}{k} - \frac{3}{4}\right)\right]\cdots. \qquad (60)$$

The similarity between this relation and equation (35) is obvious. It will be observed, however, that instead of the nuclear charge N we have an "effective nuclear charge" which is $N - \gamma$ as a first approximation and $N - \delta$ for the fine structure effect. The constant γ is known as the "total screening constant." It represents the effect of the inner electrons in neutralizing the positive charge which governs the motion of an electron rotating in an orbit outside these. The constant δ is another screening constant which is in general less than γ.

The values of W for different levels may be obtained by observations of the X-ray absorption limits (see previous section). From these, by plotting

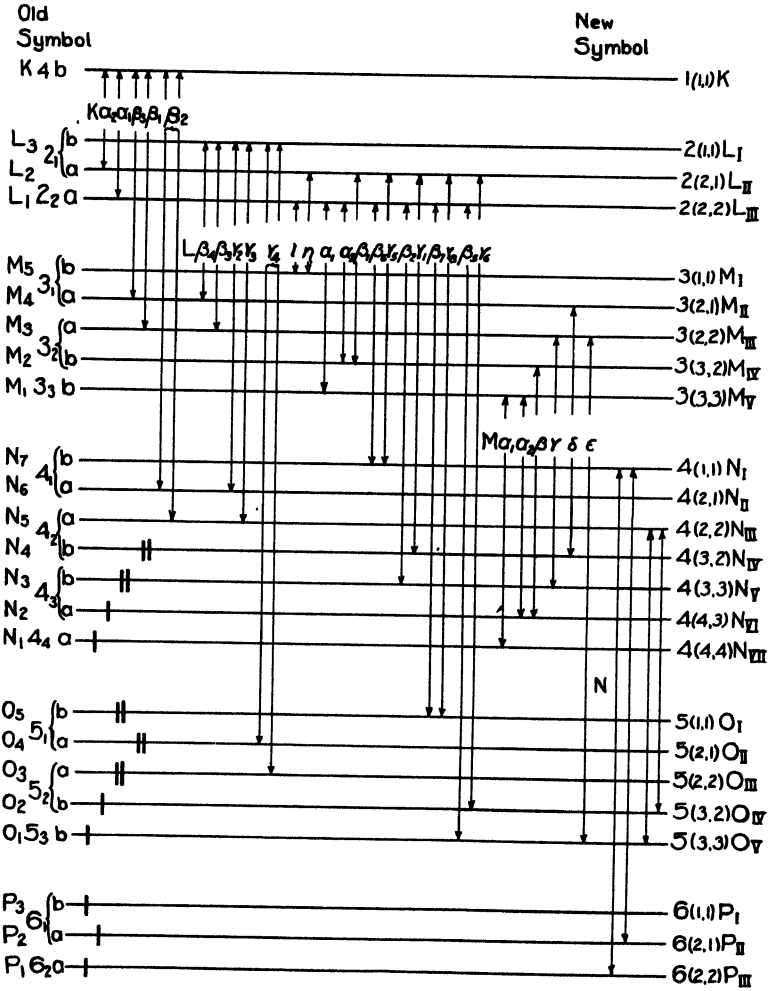


FIG. 18. Energy Levels in Radon

$\sqrt{W/R}$ against N, or (what amounts to the same thing) plotting $\sqrt{\nu/R}$ against N, it is possible to determine n and k. In this manner, as has been pointed out by Bohr, information is obtained about the configuration of the electronic orbits in the interior of the atom.

Fig. 18 shows the energy levels for the rare gas radon (Rn = 86) as deduced from X-ray absorption data for elements of high atomic number.[1] The new symbols suggested by Bohr and Coster are given at the right-hand side, while the older nomenclature is given on the left. The arrows indicate different possible transitions and correspond therefore to observed lines in the X-ray spectra. For elements of lower atomic weight the number of levels obviously decreases until in hydrogen and helium we have only one.

It has been possible to connect the occurrence of every spectral term with the presence of an electron moving in an orbit of a definite type, to the removal of which this term is supposed to correspond. That in general there corresponds more than one curve to each type of orbit n_k is due to a complication in the spectra which would lead us too far afield to enter into here, and may be attributed to the deviation from the previously described simple type of motion of the electron arising from the interaction of the different electrons within the same group.

Fig. 19, which is also taken from the paper by Bohr and Coster, shows the values of $\sqrt{W/R}$ for the different levels plotted against the corresponding values of N.

"The intervals in the system of the elements, in which a further development of an inner electron group takes place because of the entrance into the normal atom of electron orbits of a certain type, are designated in the figure by the horizontal lines, which are drawn between the vertical lines to which the quantum symbols are affixed. It is clear that such a development of an inner group is everywhere reflected in the curves. Particularly the course of the N- and O-curves may be regarded as a direct indication of that stage in the development of the electron groups with 4-quantum orbits of which the occurrence of the rare earths bears witness. Although the apparent complete absence of a reflection in the X-ray spectra of the complicated relationships exhibited by most other properties of the elements was the typical and important feature of Moseley's discovery, we can recognize, nevertheless, in the light of the progress of the last years, an intimate connection between the X-ray spectra and the general relationships between the elements within the natural system."

Fig. 20 illustrates Bohr's ideas as to the process by which an electron is bound to a nucleus.[2] This diagram shows the stationary states concerned in the emission of the arc spectrum of potassium, and it may therefore be considered as representing the process whereby the 19th electron is bound after eighteen previous electrons have already been bound in their normal orbits.

[1] Bohr and Coster, *Z. Physik.*, **12**, 342 (1923).

[2] Supplement to Nature, July 7, 1923; also, an excellent discussion of the same points has been given by J. C. McLennan, *Brit. Ass. Rep.*, Liverpool, 1923.

In the normal atom this last-bound electron occupies a 4_1 orbit. The states 4_1, 5_1, 6_1 give rise to the σ terms in the arc spectrum; states 4_2, 5_2, 6_2 give rise to the π terms while 3_3, 4_3, $\cdots$ correspond to δ terms. In the figure no attempt

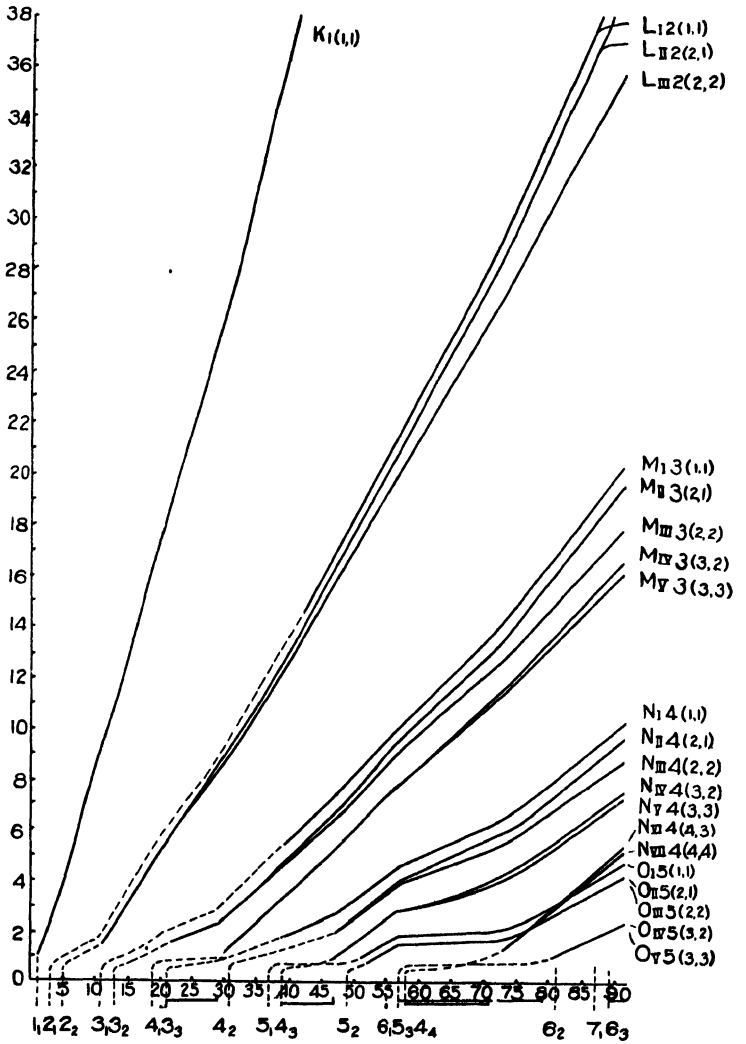


FIG. 19. $\sqrt{W/R}$ against N

is made to show the orbits of the inner electrons, but the region in which they move is enclosed by a dotted circle.

"While for the initial states of the binding process, where the quantum numbers are large, the orbit of the last electron captured lies completely out-

side of those of the previously bound electrons, this is not the case for the last stages. Thus, in the potassium atom, the electron orbits with subordinate quantum numbers 2 and 1 will, as indicated in the figure, penetrate partly into the inner region. Because of this circumstance, the orbits will deviate very greatly from a simple Kepler motion, since they will consist of a series of successive outer loops that have the same size and form, but each of which is turned through an appreciable angle relative to the preceding one. Of these outer loops only one is shown in the figure. Each of them coincides very nearly with a piece of a Kepler ellipse, and they are connected, as indicated, by a series of inner loops of a complicated character in which the electron approaches the nucleus closely. This holds especially for the orbit with subordinate quantum number 1, which, as a closer investigation shows, will approach nearer to the nucleus than any of the previously bound electrons.

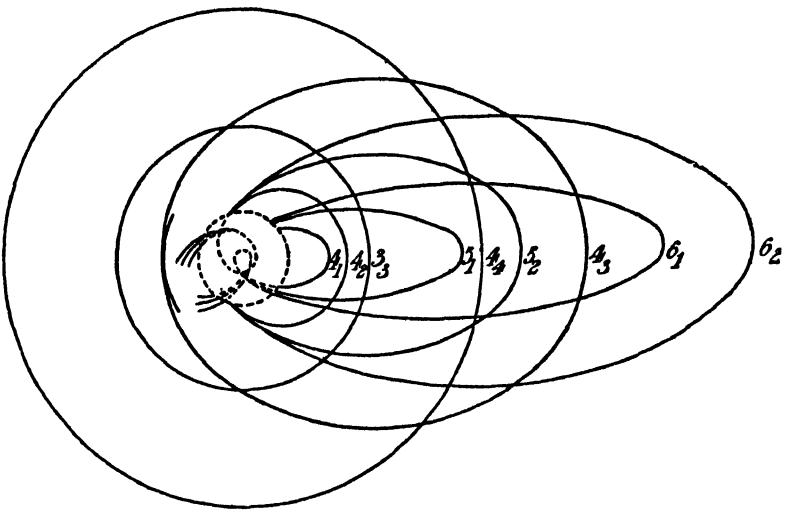


FIG. 20. Formation of Potassium Atom

"On account of this penetration into the inner region, the strength with which an electron in such an orbit is bound to the atom will—in spite of the fact that for the most part it moves in a field of force of the same character as that surrounding the hydrogen nucleus—be much greater than for an electron in a hydrogen atom that moves in an orbit with the same principal quantum number, the maximum distance of the electron from the nucleus at the same time being considerably less than in such a hydrogen orbit. As we shall see, this feature of the binding process in atoms with many electrons is of essential importance in order to understand the characteristic periodic way in which many properties of the elements as displayed in the natural system vary with the atomic number."

TABLE XIV

ELECTRONIC ORBITS IN ATOMS OF THE ELEMENTS

N \ n_k	1_1	2_1 2_2	3_1 3_2 3_3	4_1 4_2 4_3 4_4	5_1 5_2 5_3 5_4 5_5	6_1 6_2 6_3 6_4 6_5 6_6	7_1 7_2
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 (1)					
— —	—	— —					
10 Ne	2	4 4					
11 Na	2	4 4	1				
12 Mg	2	4 4	2				
13 Al	2	4 4	2 1				
— —	—	— —	— —				
18 A	2	4 4	4 4				
19 K	2	4 4	4 4	1			
20 Ca	2	4 4	4 4	2			
21 Sc	2	4 4	4 4 1	(2)			
22 Ti	2	4 4	4 4 2	(2)			
— —	—	— —	— — —	—			
29 Cu	2	4 4	6 6 6	1			
30 Zn	2	4 4	6 6 6	2			
31 Ga	2	4 4	6 6 6	2 1			
— —	—	— —	— — —	— —			
36 Kr	2	4 4	6 6 6	4 4			
37 Rb	2	4 4	6 6 6	4 4	1		
38 Sr	2	4 4	6 6 6	4 4	2		
39 Y	2	4 4	6 6 6	4 4 1	(2)		
40 Zr	2	4 4	6 6 6	4 4 2	(2)		
— —	—	— —	— — —	— — —	—		
47 Ag	2	4 4	6 6 6	6 6 6	1		
48 Cd	2	4 4	6 6 6	6 6 6	2		
49 In	2	4 4	6 6 6	6 6 6	2 1		
— —	—	— —	— — —	— — —	— —		
54 X	2	4 4	6 6 6	6 6 6	4 4		
55 Cs	2	4 4	6 6 6	6 6 6	4 4	1	
56 Ba	2	4 4	6 6 6	6 6 6	4 4	2	
57 La	2	4 4	6 6 6	6 6 6	4 4 1	(2)	
58 Ce	2	4 4	6 6 6	6 6 6 1	4 4 1	(2)	
59 Pr	2	4 4	6 6 6	6 6 6 2	4 4 1	(2)	
— —	—	— —	— — —	— — — —	— — —	—	
71 Lu	2	4 4	6 6 6	8 8 8 8	4 4 1	(2)	
72 Hf	2	4 4	6 6 6	8 8 8 8	4 4 2	(2)	
— —	—	— —	— — —	— — — —	— — —	—	
79 Au	2	4 4	6 6 6	8 8 8 8	6 6 6	1	
80 Hg	2	4 4	6 6 6	8 8 8 8	6 6 6	2	
81 Tl	2	4 4	6 6 6	8 8 8 8	6 6 6	2 1	
— —	—	— —	— — —	— — — —	— — —	— —	
86 Rn	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	
87 —	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	1
88 Ra	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	2
89 Ac	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 1	(2)
90 Th	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 2	(2)
— —	—	— —	— — —	— — — —	— — —	— — —	—
— —	—	— —	— — —	— — — —	— — —	— — —	—
118 ?	2	4 4	6 6 6	8 8 8 8	8 8 8 8	6 6 6	4 4

In Table XIV is given a summary of Bohr's conclusions [1] regarding the quantum designations and grouping of the orbits in the various atoms. The first column gives the atomic number, and the symbol at the head of each column gives the values of the quantum numbers n and k.

We have already discussed the structure of hydrogen and helium atoms. Bohr's conception of the latter is shown in Fig. 21.[2] That the third electron must occupy a 2_1 orbit is deduced from the value of the limiting frequency in the principal series for lithium. This frequency may be observed by viewing a column of lithium vapor against a continuous background, or by measuring the ionization potential of the vapor. For lithium this is 5.37 volts, while for hydrogen and helium it is 13.54 and 24.5 volts respectively. This means that the last electron is much less firmly bound than the two added previously, and we therefore understand how it is that lithium is electro-positive and univalent.

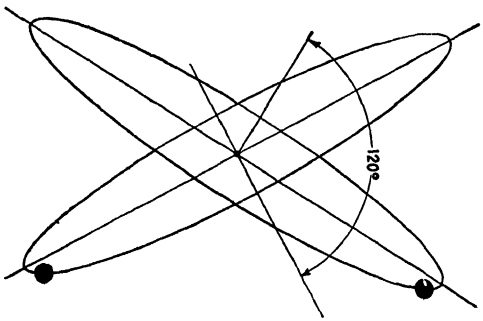


FIG. 21. Helium (2)

The model of the lithium atom as derived from spectroscopic data is shown in Fig. 22. "On account of the perturbing effect of the two inner electrons, the orbit of the valence electron is a precessing ellipse, as is true for all the orbits in complicated atoms." [3]

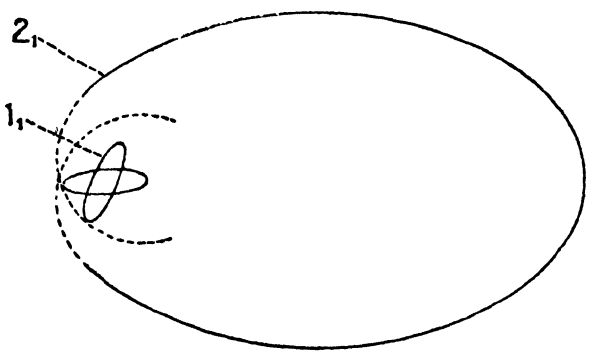


FIG. 22. Lithium (3)

As regards the *fourth, fifth* and *sixth* electrons in the atom, Bohr assumes that these are also bound in 2_1 orbits. Fig. 23 shows the structure of carbon

[1] *Nature*, July 7, 1923; also McLennan, Fig. 9, p. 10.

[2] This and the following figures are taken from the paper by Kramers, *Naturwissenschaften*, **11**, 550 (1923). The same figures are also given in Foote's paper.

[3] Foote, *loc. cit.*

atom. The symmetrical tetrahedral arrangement of the orbits is in accord with the chemical properties of this element. "Thus we shall expect that the fourth, fifth and sixth electrons in a similar way to the third will at certain moments of their revolution enter into a region where the first two bound electrons move. We must not imagine, however, that these visits with the inner system take place at the same time, but that the four electrons visit the nucleus separately at equal intervals of time." Bohr points out that "the characteristic feature of a structure like that I have suggested is the *intimate coupling between the motions of the electrons in the various groups* characterized by different quantum numbers, as well as the *greater independence in the mode of binding within one and the same group of electrons* the orbits of which are characterized by the same quantum number." [1]

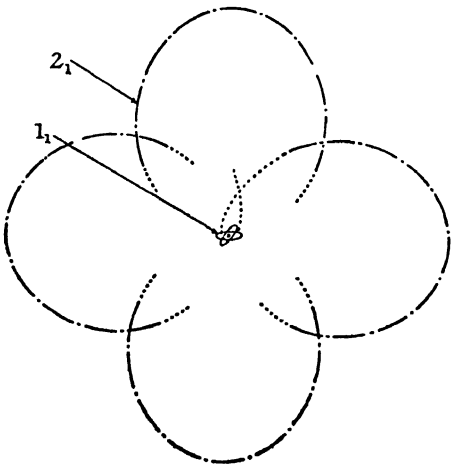


FIG. 23. Carbon (6)

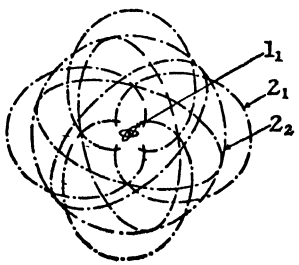


FIG. 24. Neon (10)

As more electrons are added, these assume 2_2 orbits until four more are added and the highly symmetrical neon structure (Fig. 24) is obtained.

"The symmetry of the configuration in the neon atom would be essentially, if not entirely, destroyed by the addition of another electron in an orbit of the same type as that in which the last captured electrons were bound." The ionization potential for sodium is (5.12), even less than that for lithium. Consequently the eleventh electron must be less firmly held than the third electron. This leads to the assignment of a 3_1 elliptical orbit for the valence electron in sodium (Fig. 25), a conclusion which is in agreement with the spectral series and chemical properties of this element.

Electrons are now added in 3-quanta orbits until finally in argon we have an arrangement of four 3_1 and four 3_2 orbits which resembles the structure of neon (see Fig. 26).

[1] Bohr, Atomic Structure, p. 92.

With potassium a 4_1 orbit is added. This orbit penetrates into the interior region of the atom so that at perihelion it approaches nearer the nucleus than any of the electrons previously bound in orbits of greater energy and actually coincides in this region very closely with a 3_1 orbit. This is due to the fact

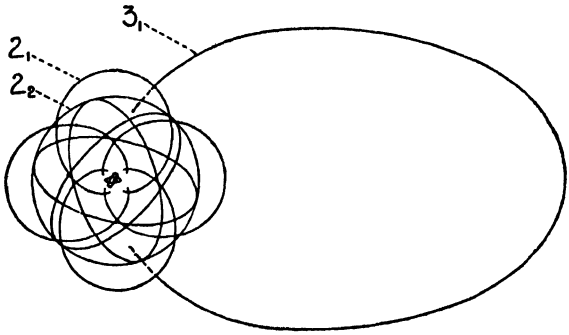


FIG. 25. Sodium (11)

that when the electron is near the nucleus it is acted upon by practically the whole charge on the nucleus. *With increasing atomic number a point is therefore reached where a 3_3 orbit corresponds to a firmer binding of the 19th electron than a 4_1*

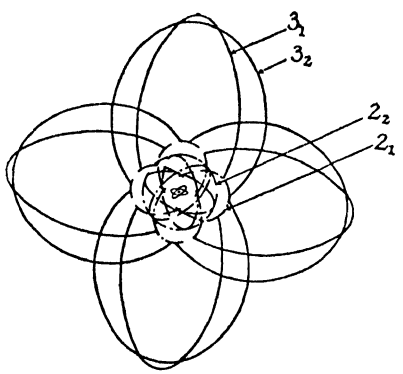


FIG. 26. Argon (18)

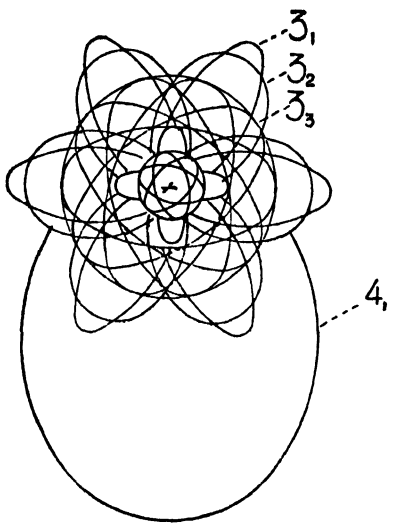


FIG. 27. Copper (29)

orbit. This occurs in the case of scandium. "A transition stage is thus initiated through which the underlying 3-quanta group of orbits is developing from two groups of four to three groups of six, with minor changes in the outer shell containing the 4-quanta orbits. In this fourth period of the periodic table

we have for the first time successive elements of similar chemical behavior, iron, cobalt, and nickel, which fact is attributable to the development of the under structure while the outer structure effective in chemical reactions remains substantially unchanged. With copper ($N = 29$), see Fig. 27, the transition stage is closed and the last electron revolves in a 4_1 orbit like potassium. However, the binding of the next to the last electron is not nearly so firm as for potassium, as is evidenced by the ease with which the spark lines of copper are excited, so that an electron in a 3_3 orbit may be readily removed. This accounts for the appearance of copper in both the cupric and cuprous forms.

"Succeeding elements in this period are built by the addition of electrons in the 4-quanta shell until the period is closed with the symmetrical configuration for krypton (36), which has an outer group of eight electrons, four each in 4_1 and 4_2 orbits respectively as shown by Fig. 28.

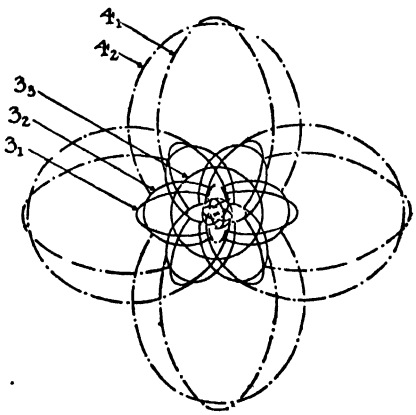


FIG. 28. Krypton (36)

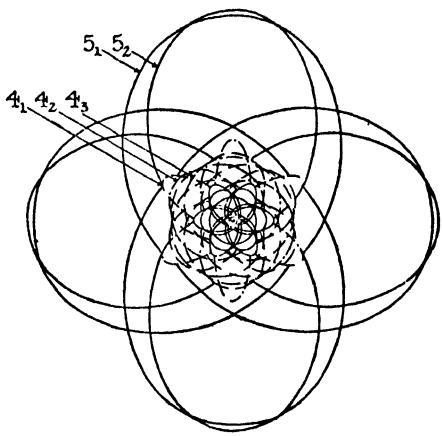


FIG. 29. Xenon (54)

"The 5th period involves transitions quite similar to those in the preceding period. The valence electron for rubidium revolves in a 5_1 orbit, but preceding silver we have a stage where the 4-quanta orbits in the underlying shell are developing from three groups of four to three groups of six, which accounts for the similarity of ruthenium, rhodium, and palladium. The period is closed with the rare gas xenon, Fig. 29, again a symmetrical structure with an outer group of eight electrons.

"The sixth period initiates the building of 6-quanta orbits. The last added or valence electron in cæsium occupies a 6_1 orbit; the two valence electrons of barium also revolve in 6_1 orbits. Beginning with lanthanum the underlying 5-quanta shell is developed, and with the next element, cerium, the first step toward the *completion* of the 4-quanta shell is initiated. Transitions in such a deep-lying level can produce but small variation as far as the chemical properties are concerned, and this group of elements where there is a develop-

ment from three groups of six to four groups of eight 4-quanta orbits is evidenced in the periodic table by the rare earths. Bohr's theory would predict that 14 elements should follow lanthanum, having about the same general chemical properties and belonging with lanthanum to the third group of the periodic table. With the last element in this group, lutecium, of atomic number 71, the underlying 4-quanta orbits are completely filled. In the building of the next element, the 72d electron must revolve in an outer orbit and hence we should expect a marked change in the chemical properties, and the 72d element should belong to Group IV, thus resembling zirconium.

"In fact if this, until recently undiscovered, element had proven to be a rare earth with the valence 3, as was frequently maintained, a rather serious difficulty for Bohr's theory would have arisen. The 73d element, tantalum, has a valence of 5 and accordingly possesses 5 comparatively loosely bound electrons in the outer shell. Thus, if there were 5 loosely bound electrons in the 73d element and only 3 loosely bound electrons in the 72d element, one of the closely bound electrons, the 69th, in the building of element 72 would be changed to a loosely bound electron in element 73. But the theory requires that the 69th (and any particular) electron be bound more firmly in every succeeding atom because of the increase in the nuclear charge. The 69th and following electrons in the 72d element should be therefore loosely bound and the element should possess a valence of 4.

"Bury was led independently to this conclusion on the basis of symmetry in the static atom so that the prediction of the chemical properties of the missing element by no means can be uniquely credited to the Bohr theory, as is sometimes stated. However, Bohr's work gave stimulus to investigation with the result that Coster and Hevesy, by means of X-ray analysis, found the 72d element associated with zirconium-bearing minerals as predicted. The new element has been named hafnium (Hf) in honor of Bohr's native city Copenhagen, and large quantities of the material have been isolated by Hevesy. In fact, it is astonishing that the discovery of this element has been so long delayed, for Hevesy estimates that it represents 1/100,000 of the earth's crust and is therefore more plentiful than lead, tin, and many other metals of commerce."

The elements between hafnium and gold are similar to those between zirconium and copper and the sixth period is completed by radon (Rn = 86) the outer structure of which resembles that of the other rare gases.

Comparison of Static Atom and Bohr Atom: In the quotation from Foote's summary, attention was drawn to the similarity between Bury's ideas on atomic structure and those of Bohr. Bury modified Langmuir's theory by assuming that instead of 2, 8, 18 or 32 electrons in the outer layer, the maximum number of electrons in this layer cannot exceed 8. "More than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18, or from 18 to 32, there occurs a transition series of elements which can have more than one structure." On the basis of this postulate and considering the

chemical properties of the elements, Bury arrives at arrangements of electrons in different shells which are in agreement with Bohr's classification of the electronic orbits. The difference between the two theories consists in the fact that where Bohr derives electronic orbits of quantum number 2, say, Bury assumes that these electrons are all arranged in the L-shell. Similarly, Bohr's group of electrons of quantum number 3 is expressed in terms of Bury's theory as constituting the M-shell. Thus the latter arrives at the following structures for the rare gases.

Element	Shell						
	K	L	M	N	O	P	Q
He...	2						
Ne ..	2	8					
Ar....	2	8	8				
Kr..	2	8	18	8			
Xe .	2	8	18	18	8		
Rn .	2	8	18	32	18	8	

Undoubtedly Bohr's theory possesses many advantages over those based on purely chemical considerations as represented by the views of Lewis, Langmuir and Bury. The attitude of most chemists at present towards Bohr's theory has probably been expressed correctly by Lewis in his recent book on Valence.[1]

"It seems to me that by this step (that is, by assigning to each electron its separate orbit) Bohr has removed every essential element of conflict between the views of the physicist and the chemist. If we regard as the important thing the orbit as a whole, and not the position of the electron within the orbit, and if each electron is assigned an independent orbit, then we may think of each electron orbit as having a fixed position in space."

Concluding Remarks

In the summary of Bohr's theory given in the present chapter little or no mention has been made of certain fundamental conceptions of the significance of the quantum theory which Bohr has applied in deriving his conclusions on the nature of the orbits in the different atoms.

In Bohr's first postulate the existence of certain stationary states is postulated. The problem regarding the criteria by which these states may be determined in any given instance has been treated by Bohr, Sommerfeld and others by the aid of certain general conceptions involving the mechanical principle of least action. The condition that the angular momentum of the electron shall be an integral multiple of $h/2\pi$ is an illustration of a particular application of this principle.

[1] Valence and the Structure of Atoms and Molecules, p. 56.

In the second postulate there are involved certain questions regarding the theory of radiation and among the most fruitful of the principles utilized by Bohr is the Adiabatic Hypothesis of Ehrenfest.[1] Briefly stated, this hypothesis asserts that if we consider an electron rotating in a given orbit of quantum number n and subject this electron to a continually and slowly changing magnetic or electrostatic field, energy of the electron in its orbital motion and the frequency of the revolution may be changed (Zeeman and Stark effects), but the value of the quantum number n defining its energy undergoes no modification.

Bohr's theory has been extended to the explanation of band spectra in terms of quantized molecular rotations. It may, in the near future, even be possible to treat chemical reactions as transitions between stationary states defined by certain quantum numbers and energy levels. The views initiated by Bohr have affected fundamentally all our previous ideas on atomic structure and radiation phenomena. But this is only a beginning and there is still with us the whole field of chemical phenomena in which there is plenty of scope for the extension of the same conceptions, and the results achieved in this manner will no doubt be just as wonderful and epoch-making as those already accomplished in the above-mentioned fields of investigation.

[1] *Die Naturwissenschaften*, 11, 543 (1923).

CHAPTER XVII

THE THIRD LAW OF THERMODYNAMICS AND THE CALCULATION OF CHEMICAL CONSTANTS

BY WORTH H. RODEBUSH, PH.D.,

Professor of Physical Chemistry, University of Illinois

The first and second laws of thermodynamics lead to the fundamental equation

$$\Delta F = \Delta H + T\left(\frac{\partial \Delta F}{\partial T}\right)_p, \tag{1}$$

where ΔF is the increase in free energy of a reaction and ΔH the increase in "heat content," at constant temperature and pressure. Since we are usually concerned with processes taking place at constant pressure, we may treat ΔF and ΔH in the above equation as functions of the temperature alone and as such we may integrate the equation. This may be done as it stands by separating the variables but a simpler method is to make use of the relation

$$\left(\frac{\partial \Delta F}{\partial T}\right)_p = -\Delta S, \tag{2}$$

where ΔS is the increase in entropy of the reaction. ΔS in turn may be expressed as a function of the temperature at constant pressure by the equation

$$\Delta S = \int_0^T \frac{\Delta C_p dT}{T} + I_0, \tag{3}$$

where ΔC_p is the sum of the heat capacities of the products of the reaction minus the sum of the heat capacities of the reacting substances, the subscript (p) indicating here as elsewhere that the quantity is measured at constant pressure. If we substitute in (1), we obtain

$$\Delta F = \Delta H - T\int_0^T \frac{\Delta C_p dT}{T} - I_0 T. \tag{4}$$

It will be noticed from equation (3) that I_0, the constant of integration, is really the change in entropy of the reaction at absolute zero and it is with this constant of integration that the Third Law of Thermodynamics is concerned.

The mathematician is wont to feel that his task is completed when he has integrated an expression. He is seldom concerned with the constant of integration. Even the physicist has been inclined to regard the constants of integration, which appear in his equations describing natural phenomena, as

haphazard quantities of no particular significance. From the practical standpoint, however, the constant of integration in equation (3) is of fundamental importance. The heat of a reaction is readily measured and is known for most reactions. The specific heats have been measured for many substances and ΔC_p as a function of the temperature can be estimated for many reactions; but, without the value of the constant I_0, these data are useless, either to tell the engineer how much work the reaction will do, or to tell the chemist whether the reaction will go. The quest of the relation of the "driving force" of a reaction to the change in total energy of the reaction has engaged the attention of students of thermodynamics for a long time. It was formerly thought that the free energy change of a reaction was equal to the total energy change. Berthelot stated this as a fundamental principle. The Kelvin rule relating the electromotive force of a galvanic cell to the heat of the reaction is another example of this error. (See Chapter II, p. 42.) Some of the chemical reactions which were first investigated appeared to confirm this view, but more accurate investigations showed that the rule was only the roughest sort of an approximation. Nevertheless, the data indicated that the relation between ΔF and ΔH is not wholly haphazard and Le Chatelier [1] in 1888 integrated the free energy equation and expressed the opinion that the time would come when we should be able to calculate the value of the constant I_0 from the known physical properties of the substance participating in a reaction. This appears to be the first recognition of a principle that is gaining favor with physicists today; viz., that in a universe made up of matter which is fundamentally homogeneous the constants of nature must be all predetermined and interrelated. This view will be further impressed upon us when we come to consider the statistical basis of thermodynamics.

After Le Chatelier, the question of the integration constant received further attention from G. N. Lewis,[2] Richards,[3] van't Hoff [4] and Haber.[5] In particular, Richards showed that for a number of galvanic cells the values of ΔF and ΔH when concentration effects were excluded approached each other as the temperature is lowered. The greatest impetus to this line of investigation, however, was given by Nernst [6] in 1906 when he published his celebrated "heat theorem." Nernst acknowledges his indebtedness to the work of his predecessors in this field, especially to Le Chatelier and Richards, but he was the first to formulate a definite hypothesis.

[1] *Ann. Mines*, **13**, 157 (1888).

[2] *Proc. Am. Acad.*, **35**, 3 (1899).

[3] *Z. physik. Chem.*, **42**, 129 (1902).

[4] Boltzman Festschrift, p. 233, Barth, Leipzig (1904).

[5] Thermodynamik technischer Gasreaktionen, Oldenbourg, Munich, 1905.

[6] *Nachr. kgl. Ges. Wiss. Gottingen, Math.-Phys. Klasse*, 1 (1906). *Die theoretischen und experimentallen Grundlagen des neuen Wärmesatzes*, Halle (1918).

The Nernst Heat Theorem

Inspection of equation (1) shows that, unless $\left(\frac{\partial \Delta F}{\partial T}\right)_p$ be infinite, ΔF must equal ΔH at 0° K., since $T = 0$. The two quantities might approach each other in the manner indicated by the curves (I), Fig. 1. From a study of cases of the type discussed by Richards, however, Nernst was led to assume that the values of ΔF and ΔH approach each other asymptotically, (II), Fig. 1, and become identical at absolute zero for reactions in condensed systems, i.e., solids or liquids. This statement may be expressed mathematically by saying that

$$\lim_{T=0} \frac{d\Delta F}{dT} = \lim_{T=0} \frac{d\Delta H}{dT} = 0. \qquad (5)$$

Since

$$\frac{d\Delta F}{dT} = -\Delta S \quad \text{and} \quad \frac{d\Delta H}{dT} = \Delta C_p,$$

we then have

$$\lim_{T=0} \Delta S = \lim_{T=0} \Delta C_p = 0 \qquad (6)$$

at 0° K., or from (3)

$$I_0 = 0. \qquad (7)$$

Hence, we may insert or remove at our pleasure the limit $T = 0$ in any integral of ΔC_p with respect to temperature.

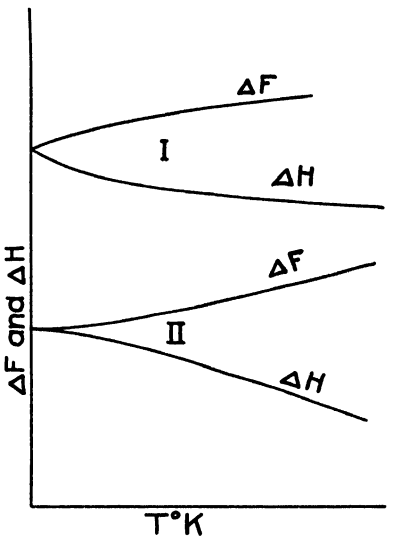


Fig. 1

This appears to be a remarkably simple conclusion and one which should be easily arrived at, but the experimental verification which is necessary to establish the truth or falsity of so general an assumption is a matter of many years work.

Let us consider a reaction at a given temperature between solid substances

$$A_S + B_S \rightarrow C_S.$$

Each phase may be assumed to have a vapor pressure represented by P with the appropriate subscript. If the vapor pressure be small so that the vapor behaves as a perfect gas and the volume of the solid may be neglected, we may use the Clapeyron equation

$$\frac{dlnP}{dT} = \frac{\Delta H}{RT^2}, \qquad (8)$$

where ΔH is the heat of vaporization at constant pressure at the temperature in question. We can integrate this if we express ΔH as a function of the

temperature

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_p dT, \tag{9}$$

where ΔC_p is the heat capacity of the vapor minus the heat capacity of the solid. Integrating,

$$lnP = -\frac{\Delta H_0}{RT} + \int \frac{\int_0^T \Delta C_p dT}{RT^2} dT + i. \tag{10}$$

We can integrate the third term of (10) by parts,

$$\int \frac{\int_0^T \Delta C_p dT}{RT^2} dT = -\frac{\int_0^T \Delta C_p dT}{RT} + \int \frac{\Delta C_p dT}{RT}.$$

Combining with (9) and substituting in (10), we have for P_A

$$lnP_A = -\frac{\Delta H_A}{RT} + \int \frac{\Delta C_{pA} dT}{RT} + i_A. \tag{11}$$

Similar expressions hold for lnP_B and lnP_C.

Let us now suppose that A and B are vaporized and react to form the vapor of C which is then condensed to form the solid. At equilibrium in the vapor phase we have the mass law

$$\frac{p_C}{p_A p_B} = K_p, \tag{12}$$

where p_A, p_B, p_C are the partial pressures at equilibrium as distinguished from the vapor pressures of the solid phases. We have the well-known relation

$$\frac{dlnK_p}{dT} = \frac{\Delta H_R}{RT^2}, \tag{13}$$

where ΔH_R is the heat of reaction in the gaseous phase at constant pressure. This equation may be integrated precisely as (8) above, with similar assumptions, and we obtain

$$lnK_p = -\frac{\Delta H_R}{RT} + \int \frac{\Delta C_{pR} dT}{RT} + i_R. \tag{14}$$

Here

$$\Delta C_{pR} = C_{pC(\text{gas})} - C_{pA(\text{gas})} - C_{pB(\text{gas})}.$$

Now the change in free energy in carrying out the reaction in steps as indicated above is given by the equation

$$\Delta F = RTln\frac{p_A}{P_A} + RTln\frac{p_B}{P_B} + RTln\frac{P_C}{p_C}. \tag{15}$$

Since

$$\frac{p_C}{p_A p_B} = K_p,$$

this may be written

$$\Delta F = RT(lnP_C - lnP_A - lnP_B - lnK_p). \tag{16}$$

If we substitute the expressions for lnP_C, etc., and lnK_p from equations (11) and (14), we obtain

$$\Delta F = RT\left[\frac{-\Delta H_C + \Delta H_A + \Delta H_B + \Delta H_R}{RT} + \int \frac{(\Delta C_{pC} - \Delta C_{pA} - \Delta C_{pB} - \Delta C_{pR})}{RT} dT + i_C - i_A - i_B - i_R\right]. \tag{17}$$

But

$$-\Delta H_C + \Delta H_A + \Delta H_B + \Delta H_R = \Delta H_S,$$

where ΔH_S is the heat of reaction for the solid phase. Likewise,

$$-(\Delta C_{pC} - \Delta C_{pA} - \Delta C_{pB} - \Delta C_{pR}) = \Delta C_{pS},$$

the heat capacity of solid C minus the heat capacities of solids A and B. ΔF must also be equal to the free energy change of the reaction between the solid phases. Hence we have

$$\Delta F = \Delta H_S - T\int_0^T \frac{\Delta C_{pS} dT}{T} + (i_C - i_A - i_B - i_R)RT. \tag{18}$$

From this equation we see that the constant of the free energy equation for the reaction

$$A_S + B_S \rightarrow C_S$$

is equal to the algebraic sum of the constants for the separate stages by which the reaction may proceed. And in general it follows that if any chemical reaction is equivalent to the sum of two other reactions, the constant of integration of the equation for the change of free energy in the first reaction is equal to the algebraic sum of the constants of the equations for the change of free energy in the other reactions.

The above statement was demonstrated by Le Chatelier. He pointed out also that the constants of integration for reactions of the same type would have approximately the same numerical value. Thus, if we integrate the Clapeyron equation, neglecting the change in ΔH, we get

$$lnp = -\frac{\Delta H}{RT} + I. \tag{19}$$

This gives us Trouton's rule for the relation between the heat of vaporization and the boiling point when $p = 1$ atm., the value of I for many liquids being approximately 11, which gives

$$\frac{\Delta H}{T} = 22$$

at the boiling point. Similar regularities have been found in the constants for dissociation of solids and combinations of hydrogen and the halogens.

If we compare equation (18) with (4), we see that

$$R(i_C - i_A - i_B - i_R) = -I_0,$$

and since by (7)

$$I_0 = 0,$$

$$I_R = i_R \cdot R = (i_C - i_A - i_B)R. \tag{20}$$

By the Nernst assumption, therefore, the constant of integration of the free energy equation for a reaction between substances in the vapor phase is equal to the algebraic sum, multiplied by R, of the constants in the vapor pressure equations for the substances in the solid state. Furthermore, since the constant of the vapor pressure equation measures a property of the vapor, it is independent of the nature of the condensed phase. Thus, the vapor pressure equation for liquid water will have the same constant as the vapor pressure equation for ice. Nernst hoped to determine the values of the constant of equation (10) from vapor pressure data and from these to calculate free energies from heats of reaction. He avoided serious errors in the integration of the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H}{(V - V_0)T} \tag{21}$$

at high pressures by the use of the relation

$$p(V - V_0) = RT\left(1 - \frac{p}{\pi}\right), \tag{22}$$

where π is the critical pressure. Unfortunately, however, he attempted to extrapolate empirical equations for heat capacities to low temperatures. Furthermore, since most substances with measurable vapor pressures are liquids, he made the extrapolations for the liquid phase and the thermal properties of liquids behave in a very anomalous manner at low temperatures.

From his inspection of the vapor pressure data for a number of liquids Nernst came to the conclusion that the heat capacities of all condensed phases approached a limiting value at 0° K. of 1.5 calories per gram atom. For gases he assumed

$$C_p = 3.5 + 1.5\eta,$$

where η is the number of atoms per molecule. He then represented heat of vaporization as a function of the temperature by the empirical equation

$$\Delta H = (\Delta H_0 + 3.5T - \epsilon T^2)\left(1 - \frac{p}{\pi}\right), \tag{23}$$

where ϵ is a constant characteristic of the substance. By combining (23) with (21) and (22), integrating and changing to common logarithms, we get instead of equation (10)

$$\log p = \frac{-\Delta H_0}{4.58T} + 1.75 \log T - \frac{\epsilon T}{4.58} + C. \tag{24}$$

The constant C of this equation Nernst has termed the "conventional chemical constant." By this terminology he recognizes the approximate nature of equation (24) as distinguished from equation (10) which is an exact thermodynamic equation. The constant i of equation (10) is termed the "true" chemical constant.

Experimental work initiated by Nernst himself has shown that his assumptions as to the behavior of specific heats at low temperatures are incorrect. Equation (19) is a satisfactory vapor pressure equation in the range where vapor pressures are measurable but it cannot be extrapolated to low temperatures. Unfortunately, many attempts have been made by other chemists to use the chemical constants erroneously calculated from this equation. Nevertheless, the principle announced by Nernst, when properly limited in its application, is of the most fundamental importance. The constant of equation (10) calculated from accurate specific heat data for solid substances is a useful quantity. We shall return to it later.

The Third Law of Thermodynamics

Einstein [1] predicted in 1907 that the specific heats of all substances would approach zero at the absolute zero of temperature. A little later Planck [2] stated that the entropy of pure solids or liquids was zero at 0° K. Thus, we see that, while the Nernst theorem stated that S and C_p had the same values per gram atom for all substances (the value of C_p being assumed to be 1.5 cal. at 0° K. and S being indeterminate), the conclusions of Einstein and Planck were that

$$\lim_{T=0} S = \lim_{T=0} C_p = 0.$$

For crystalline solids these conclusions have been amply verified. Postponing for the present the consideration of other forms of matter, we may state that *the entropy of every pure crystalline substance is zero at absolute zero.* This statement has been called the third law of thermodynamics and it appears to be of sufficient importance to take rank with the first and second laws.

[1] *Ann. Physik*, (4) **22**, 180 (1907).
[2] *Ber.*, **45**, 5 (1912).

It will be seen at once that the third law is inclusive of the Nernst theorem in so far as crystalline solids are concerned since if, at $T = 0°$ K.,

$$S = C_p = 0,$$

then, obviously, also at $T = 0°$ K.,

$$\Delta S = \Delta C_p = 0.$$

This view introduces entropy to us as a definite positive quantity.[1] With such quantities as free energy or total energy the case is far otherwise. We can only measure changes in energy and any assignment of actual values of energy to individual substances must be arbitrary. Thus, we may consider a crystal of sodium chloride at absolute zero. It possesses no kinetic energy and if we could find no reaction it would undergo, we might say that its total energy content was zero. But, if it were found that sodium chloride would or should react with metallic potassium at 0° K. or were capable of a radioactive decomposition, we would have to revise our statement. So, it was formerly supposed that any expression for entropy must contain an undetermined and indeterminate constant.

The difference between the entropy of a substance at a temperature T and at 0° K. is given by the relation

$$S_T - S_0 = \int_0^T \frac{C_p dT}{T}. \tag{25}$$

If C_p did not approach zero at 0° K., our integral would contain a term $-\infty$. But experimental evidence shows, approximately at least, that at very low temperatures

$$C_p = aT^3,$$

and the integral (19) becomes definite with the value zero at 0° K. Furthermore, no substances have been found to have a negative entropy in any state. Hence, the Planck assumption appears plausible from general considerations.

Experimental Verification: In the experimental verification of the third law we may follow either of two methods. We may calculate the chemical constants of Nernst from equation (10) for the substances participating in a reaction and compare them with the constant for the reaction as directly measured, or we may calculate entropies from specific heat data at low temperatures and use the relation

$$\Delta F - \Delta H = -T\Delta S$$

for reactions for which ΔF and ΔH have been measured. Obviously, the number of reactions for which we have the very complete data required will not be large.

As a matter of fact, we can show very readily that the two methods lead to the same result and we can then use the simpler. Let us consider a reaction

[1] Gibbs evidently was aware of this characteristic of entropy. See his Elementary Principles in Statistical Mechanics, p. 184, Yale University Press, New Haven, 1914.

in the gaseous phase

$$A + B \rightarrow C.$$

According to the Nernst theorem,

$$i_R = i_C - i_A - i_B,$$

where i_A, i_B, i_C are the "true chemical constants" of the vapor pressure equations for A, B, and C in the *solid* state. Substituting the values of $i_R \cdots i_B$ from equations (11) and (14),

$$ln\frac{p_C}{p_A p_B} + \frac{\Delta H_R}{RT} - \int \frac{\Delta C_{pR} dT}{RT} = lnP_C - lnP_A - lnP_B + \frac{\Delta H_C - \Delta H_A - \Delta H_B}{RT} - \int \frac{(\Delta C_{pC} - \Delta C_{pA} - \Delta C_{pB})dT}{RT}. \tag{26}$$

Multiplying through by $-RT$ and collecting the terms,

$$RTln\frac{p_A}{P_A} + RTln\frac{p_B}{P_B} + RTln\frac{P_C}{p_C} - (\Delta H_R + \Delta H_A + \Delta H_B - \Delta H_C) = -T\int \frac{\Delta C_{pS} dT}{T}. \tag{27}$$

But, by the third law,

$$\int \frac{\Delta C_p dT}{T} = \int_0^T \frac{\Delta C_p dT}{T} = \Delta S$$

and the equation (27) by comparison with (15) and (17) reduces to

$$\Delta F - \Delta H = -T\Delta S \tag{28}$$

for the reaction between the substances in the solid state. Hence, the use of chemical constants in a verification of the third law appears as a roundabout method of doing what may be done directly by substitution in equation (28). If we find that we can calculate ΔS for a reaction from heat capacity data by means of the third law assumptions, we shall verify the Nernst relation. We may do this by comparing the value of $\Delta F - \Delta H$ as directly determined with the value of $-T\Delta S$ as calculated by the integral $\int_0^T \frac{\Delta C_p dT}{T}$ for the reaction.

In 1917 Lewis and Gibson [1] collected the data for nine cases where the third law could be checked. They found an average discrepancy of 1.6 entropy units (about 475 cals. in ΔF or ΔH at 298° K.) between entropies of reaction calculated (1) from equilibrium measurements and (2) from specific heat data. In a recent paper Lewis, Gibson and Latimer [2] have been able to show that,

[1] *J. Am. Chem. Soc.*, **39**, 2554 (1917).
[2] *J. Am. Chem. Soc.*, **44**, 1008 (1922).

with more accurate data, these discrepancies have been greatly reduced. We have tabulated (Table I) those reactions for which they were able to find data sufficiently accurate to eliminate uncertainty from the calculations. In the table the values of $\Delta F - \Delta H$ are directly determined and the values of $-T\Delta S$ are calculated from specific heat data. The values given are at 298° K.

A detailed consideration of the very simple reaction

$$\text{Sn (gray)} \rightarrow \text{Sn (white)}$$

will illustrate the manner in which the calculations are made. As is well known, tin exists in two modifications, the white and the gray forms, the latter stable at low temperatures. The transition point is 19° C. Brönsted [1] has studied this reaction from the standpoint of the third law. He determined calorimetrically that, at the transition point,

$$\Delta H = 541 \text{ cal.}$$

From this value and the heat capacities of the two forms, $\Delta F - \Delta H$ at 25° C. is readily calculated. Brönsted [2] also determined the heat capacities of the two forms at liquid air temperatures. These determinations do not extend below 70° K. but, by means of the "characteristic heat capacity curve" for the metals (which we shall discuss later), we can extrapolate to 0° K. with great confidence. In order to obtain the entropy of either form, we must obtain the integral

$$\int_{T}^{T} \frac{C_p dT}{T}$$

for that form. If we plot C_p as ordinate against lnT as abscissa, the area under the curve (Fig. 6) will then represent the integral. By means of this graphical integration we obtain the values for the entropies at 298° K.,

$$\text{Sn (white)} : S = 11.17, \qquad \text{Sn (gray)} : S = 9.23, \qquad \Delta S = 1.94.$$

TABLE I

EXPERIMENTAL VERIFICATION OF THE THIRD LAW

Reactions	$\Delta F - \Delta H$ (cal.) (From equilibrium measurements)	$-T\Delta S$ (cal.) (From heat capacity data)	Difference
$Sn\ (gray) \rightarrow Sn\ (white)$	557	578	21
$S\ (rhombic) \rightarrow S\ (monoclinic)$	− 66	− 89	23
$C\ (graphite) + \frac{1}{2}O_2 \rightarrow CO$	− 6370	− 6000	370
$Hg + \frac{1}{2}O_2 \rightarrow HgO$	+ 7790	+ 7620	170
$Ag + HgCl \rightarrow AgCl + Hg$	− 2320	− 2295	25
$\frac{1}{2}Pb + AgCl \rightarrow \frac{1}{2}PbCl_2 + Ag$	+ 1280	+ 1280	0
$\frac{1}{2}Pb + AgI \rightarrow \frac{1}{2}PbI_2 + Ag$	+ 1190	+ 1100	90

[1] *Z. physik. Chem.*, **88**, 479 (1914).

[2] Rodebush [*J. Am. Chem. Soc.*, **45**, 1413 (1913)] has redetermined the heat capacity for white tin, finding slightly higher values at low temperatures. In comparing the entropies of the two forms, however, it is better to use Brönsted's figures only.

The principal uncertainty in the values for $\Delta F - \Delta H$ are in the calorimetric determination values of ΔH which are given in the literature. In the last three reactions tabulated, this source of error was avoided in an ingenious manner by Gerke.[1] He measured the temperature coefficients of the electromotive force of these reactions in galvanic cells very accurately. From these, $\Delta F - \Delta H$ can be calculated readily by the Gibbs-Helmholz equation

$$\Delta F - \Delta H = -23{,}074T\frac{dE}{dT},$$

where E is the electromotive force.

In addition to these seven cases where accurate checks are obtained, there are a large number of calculations that can be made from somewhat uncertain data which show the third law to be at least approximately true, since there are no serious discrepancies. Some of these we shall consider later. The third law is thus supported by a considerable quantity of the sort of evidence that has caused the first and second laws to be accepted as absolute.

It may develop from further experimentation that the third law is subject to additional limitations, but it seems more probable that when its application is thoroughly understood, it will be found to be a principle of the utmost generality.

The Entropy of Solutions and Supercooled Liquids

We have seen that Nernst assumed ΔS to be zero for all reactions between condensed phases. Planck [2] went one step further and stated that we should meet with no inconsistencies if we assume the entropy of every pure solid and liquid to be zero at 0° K. On the other hand, Planck concluded that the entropy of a solution would be found to be greater than zero at absolute zero. His argument is as follows. If we mix two substances of properties sufficiently alike so that they form what may be called an ideal solution, we have an increase in entropy

$$\Delta S = -n_1 R \ln N_1 - n_2 R \ln N_2, \qquad (29)$$

where n_1 and n_2 are the actual number of mols. of each of the two substances

[1] *J. Am. Chem. Soc.*, **44**, 1684 (1922). The principle of avoiding the calorimetric determination of ΔH by measuring the temperature coefficient of the cell reaction was employed by Jones and Hartmann, *J. Am. Chem. Soc.*, **37**, 752 (1915), with the cell

$$\mathrm{Ag}\left|\mathrm{AgI\ in}\ \frac{\mathrm{N}}{10}\mathrm{KI}\right|\left|\frac{\mathrm{N}}{10}\mathrm{KI}\right|\underset{\text{with Iodine}}{\overset{\text{Satd.}}{\mathrm{I_2}}}\Bigg|\mathrm{Pt}.$$

Their results were incorrect, probably due to incorrect determinations of liquid potential differences. The determination of $\Delta F - \Delta H$ by measurement of the temperature coefficient of the electromotive force is not without its own special difficulties, as pointed out by Taylor, *J. Am. Chem. Soc.*, **38**, 2308 (1916); this is also the conclusion reached by Webb, Thesis, Princeton University, 1924.

[2] *Ber.*, **45**, 5 (1912); *Warmestrahlung*, 4th ed., pp. 204–221, Barth, Leipzig.

and N_1 and N_2 are the respective mol. fractions after mixing. For a mixture of $\frac{1}{2}$ mol. of each this reduces to

$$Rln2 = 1.4$$

entropy units. Experiment shows that the specific heats of solutions are usually very close to the mean of the specific heats of the components, the more nearly so the more nearly the two constituents are alike in their properties. If such a solution be cooled down to 0° K., the integral

$$\int_0^T \frac{C_p dT}{T}$$

for the solution would not be different from the integrals

$$\int_0^T \frac{C_p dT}{T}$$

for the two pure constituents. But the entropy of the solution is greater by 1.4 than the sum of the entropies of the pure substances, and, hence, must be greater than 0 at 0° K. Since most solutions on solidification tend to separate into the pure solid constituents, the most likely manner in which a solution would be obtained at low temperature would be by rapid cooling, so that the crystalline solid would not form. Gibson, Parks and Latimer [1] obtained the specific heat curves for mixtures of ethyl and propyl alcohol down to liquid air temperature and found the curve to approximate the mean of the curves for the pure supercooled liquids. Since the entropy difference is only 1.4 units, the results were not very decisive. The specific heat curves of the supercooled liquids were of a peculiar shape, however, and a consideration of them led Lewis and Gibson [2] to predict that the entropy of a pure supercooled liquid would be considerably greater than for the pure substances. The most decisive evidence on this point is the work of Gibson and Giauque.[3] Their results for the molecular heats of amorphous and crystalline glycerol are shown in Fig. 2, where they are plotted against log T. The entropy of fusion for glycerol is 15.02 units. In order to establish the third law for supercooled liquids, the integral

$$\int \Delta C_p dlnT$$

must be equal to this. The area between the curves of the plot multiplied by 2.303 represents this integral and the value obtained is only 9.39, leaving a discrepancy of 5.63 units. The curves might again diverge at lower temperatures. Simon [4] has obtained the specific heats of amorphous glycerol down to liquid hydrogen temperatures. His results are indicated by the broken line. If the specific heat for crystalline glycerol were to drop suddenly to

[1] *J. Am. Chem. Soc.*, **42**, 1542 (1920).
[2] *J. Am. Chem. Soc.*, **42**, 1529 (1920).
[3] *J. Am. Chem. Soc.*, **45**, 93 (1923).
[4] *Ann. Physik.*, [4] **68**, 241 (1922).

zero, the value of the integral $\int \Delta C_p d\ln T$ might be increased by the necessary amount to make the third law valid. It would be very desirable to obtain further data. Wietzel [1] has obtained data on amorphous and crystalline quartz which indicates a similar discrepancy but here again the data are not sufficient. Altogether, the experimental evidence throws grave doubt on the applicability of the Nernst theorem to supercooled liquids. We shall consider the question from a theoretical standpoint later.

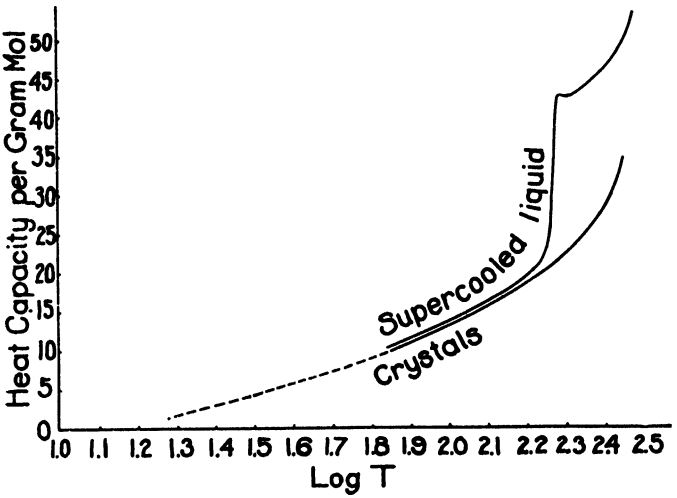


FIG. 2. Heat Capacity of Crystalline and Supercooled Liquid Glycerol

THE HEAT CAPACITY OF SUBSTANCES

Experimental Determination at Low Temperatures: Nernst realized the necessity of obtaining exact specific heat data in order to calculate chemical constants and he was one of the first to initiate work along this line. The first measurements made were of the mean specific heat of substances over considerable ranges of temperature. In order to evaluate the integral

$$\int_0^T \frac{C_p dT}{T},$$

however, it is necessary that the true specific heat be known accurately as a function of the temperature. Since the value of C_p changes rapidly with the temperature in certain ranges for most substances, it becomes necessary to measure the energy input for changes of temperature of not more than one or two degrees. The method of measurement devised by Nernst [2] has been

[1] *Z. anorg. Chem.*, 116, 71 (1921).

[2] Nernst, *J. Phys.*, (4) 9, 721 (1910); Nernst, Koref and Lindemann, *Sitz. ber. Preuss. Akad.*, 247, 262 (1910); Nernst, *Ann. Physik*, 36, 395 (1911); Eucken, *Phys. Z.*, 10, 586 (1909); Eucken and Schwers, *Sitz. ber. Preuss. Akad.*, 369 (1914); Kammerlingh Onnes and Keesom, *Proc. Amsterdam Akad.*, 894 (1914).

followed in all of the recent work at low temperatures. The substance of which the heat capacity is to be measured is placed in a container which is supplied with an electrical heating coil and a thermocouple or resistance thermometer. A measured amount of electrical energy is supplied to the heating coil and the rise in temperature is measured. In order to prevent heat exchange with the surroundings by conduction, the container is suspended in a vacuum. Radiation is prevented by wrapping the container in silver foil. Since a very high vacuum may be obtained and radiation is negligible at low temperatures, the heat leak is practically eliminated. In working with metals which may be made into a block of the desired form, the container is often eliminated.

The principal source of error in the low temperature work is to be found in the uncertainty of the temperature measurements. Below 90° K. both thermocouples and resistance thermometers behave in an anomalous manner and calibrations must be made at frequent intervals in the temperature range.[1] The principal work upon heat capacities at low temperatures has been done by Nernst and his coworkers in Germany, Kammerling Onnes in Holland, Griffiths and Griffiths in England and G. N. Lewis and his associates in America. Data are now available for most of the elements and many compounds including the common inorganic salts.

The Heat Capacity of Monatomic Solids: In a previous paragraph we referred to the "characteristic curve" for the heat capacities of the metals at low temperatures. For a large class of solid substances the atomic heat capacity at constant volume C_v may be represented by an equation of the form

$$C_v = f\left(\frac{\theta}{T}\right), \tag{30}$$

where f is the same function for all these substances and θ is a constant characteristic of the individual substance. Most of the elements and a number of the inorganic salts are included in this classification. These substances occur in the form of monatomic crystals, i.e., the unit in the crystal lattice is a single atom.

If we plot C_v for different substances against T, we get a series of curves, Fig. 3, which show little similarity. If, however, we plot C_v against log T (Fig. 4), the curves appear to be of precisely the same form, differing only in position along the log T axis. Equation (30) may be written

$$C_v = f(\log \theta - \log T),$$

from which it is evident that if the function f is the same for different substances, the curves when plotted against log T should be brought into coincidence by displacement along the log T axis. The remarkable exactness of relation (30) is shown very simply by the device employed by Lewis and Gibson [2] of plotting

[1] See Rodebush, *J. Am. Chem. Soc.*, **45**, 1413 (1923).

[2] *J. Am. Chem. Soc.*, **39**, 2560 (1917).

the heat capacity data on separate sheets of transparent paper so that the curves may be superposed. For the above-mentioned class of substances this may be done within the limits of experimental error. This is the more remarkable when we consider that the data for such widely different substances as metallic lead and carbon in the form of diamond lie on curves of the same

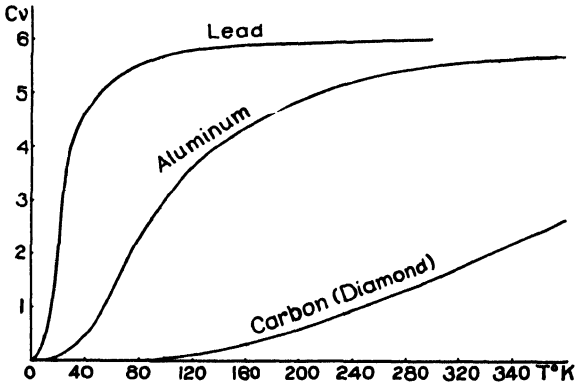


FIG. 3

form on the C_v- log T diagram. In studying the nature of this function f, we shall always find it advantageous to plot C_v against log T rather than against T.

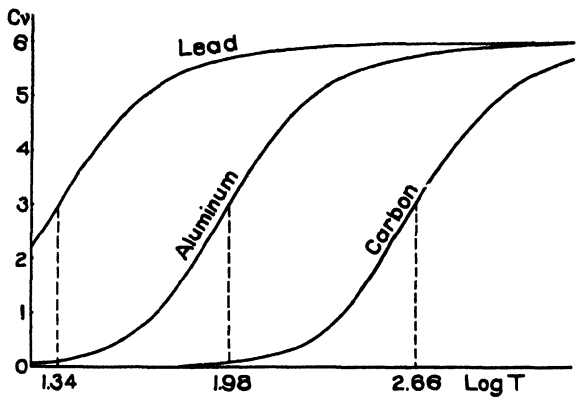


FIG. 4

In the ordinary measurement of specific heats, C_p, the heat capacity at constant pressure, is obtained. Since it is C_v that exhibits the regularities we have described, it must be calculated from C_p by the equation

$$C_v = C_p - \frac{\alpha^2 v T}{\beta}, \tag{31}$$

where α is the coefficient of expansion, β the compressibility, and v the gram atomic volume. These quantities (α and β) have been measured for most substances at room temperature but they are functions of the temperature and there is considerable uncertainty in making the calculation at low temperatures. At temperatures sufficiently low the term becomes negligible without doubt. Lindeman and Magnus [1] have proposed the empirical equation

$$C_v = C_p - aT^{3/2}, \tag{32}$$

where a is calculated at ordinary temperatures from the measured values. This equation is a very rough approximation but the total value of the correction is small.

Since the form of the heat capacity curve has been determined with great precision by Nernst,[2] Eucken,[3] Kammerlingh Onnes [4] and others, it becomes possible by obtaining a few data for C_v for a monatomic solid somewhere in the region between $C_v = 1$ and $C_v = 5$ to extrapolate for the entire curve without serious error.

Theoretical Equations for Heat Capacity: In 1907 Einstein [5] derived an equation from Planck's radiation formula for the heat capacity of a system of simple harmonic oscillators and since all forms of matter at low temperatures may be presumably regarded as made up of different sorts of these oscillators, he predicted that the heat capacity of all forms of matter would approach zero at the absolute zero. This prediction has been amply verified for all forms of real matter. The equation of Einstein is of the highest fundamental importance and we shall derive it from purely mechanical considerations with the aid of the quantum theory, avoiding the use of the theory of radiation.

By a simple harmonic oscillator we mean a particle of matter (atom, electron, etc.) which oscillates in a straight line through a point of equilibrium, the restoring force being proportional to the displacement. This condition may be expressed mathematically by the equation

$$f = -ps, \tag{33}$$

where f is the force, s the displacement and p a constant sometimes called the "constraint." Such an oscillator moves with what is known as simple harmonic motion. For a system of such oscillators the instantaneous distribution of kinetic energy according to the classical mechanics is given by the equation

$$dN = Ke^{-E/kT}\frac{dE}{\sqrt{E}}. \tag{34}$$

Here dN is the number of oscillators having energies between E and $E + dE$, E being the kinetic energy of the individual oscillator. k is the molecular

[1] Lindeman and Magnus, *Z. Elektrochem.*, **16**, 269 (1910).
[2] *Z. Elektrochem.*, **17**, 817 (1911).
[3] Eucken and Schwers, *Verh. deut. physik. Ges.*, **15**, 582 (1913).
[4] Kammerlingh Onnes, *Com. Phys. Lab.*, Leiden, No. 147 (1915).
[5] Einstein, *Ann. Physik.*, [4] **22**, 180 (1907).

gas constant, T the absolute temperature and K a constant involving the total number of oscillators.

Likewise for the potential energy [1]

$$dN = K_p e^{-E_p/kT} \frac{dE_p}{\sqrt{E_p}}. \tag{35}$$

So far as classical mechanics tells us, these two distributions are independent of each other.

From another viewpoint equations (34) and (35) represent the respective probabilities that an oscillator has kinetic and potential energies within specified limits. Now the probability that an oscillator have a given momentum and at the same time a given position is the product of the separate probabilities and, without evaluating constants, the combined distribution law becomes

$$dN = Ke^{-E/kT}dE, \tag{36}$$

where E is the total energy of the oscillator both kinetic and potential. If we represent (Fig. 5) position along the horizontal axis s and momentum along the vertical axis mv, we then have a two-dimensional cross section of a Gibbs "phase space," where the point representing the position and momentum of our oscillator at any instant travels in ellipses about the center O. Now the quantum theory assumes [2] that, for a complete oscillation, the integral of momentum times length must be an integral multiple of the Planck constant h. That is,

$$\oint mvds = nh, \tag{37}$$

where n is an integer. Since the point representing an oscillator travels around an ellipse (Fig. 5) during an oscillation, the integral represents the area of the ellipse. Reduced to its simplest terms then, the "phase point," as we shall call this representative point, is limited in its travels to a series of ellipses whose areas are integral multiples of h. It must pass from one ellipse to another by a sudden discontinuous motion or jump.

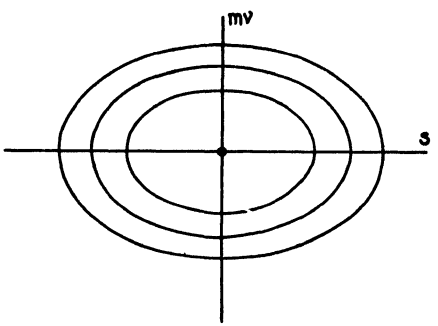


FIG. 5

The area of the nth ellipse, then, is $\pi(mV_n)S_n$, where mV_n and S_n are respectively the maximum momentum and displacement of the particle. Hence we have from our quantum assumption

$$\pi(mV)S = nh. \tag{38}$$

[1] These relations will be derived later. See page 1167 *et seq.*

[2] Sommerfeld, *Atombau und Spektrallinien*, 3 ed., p. 243, Friedr. Vieweg and Son, Braunschweig, 1922.

Since the total energy of the oscillator is constant throughout an oscillation, it may be readily expressed either in terms of the maximum displacement S when it is all potential or the maximum momentum mV when it is all kinetic,

$$E = \tfrac{1}{2}pS^2 = \tfrac{1}{2}mV^2. \tag{39}$$

Since

$$V = \sqrt{\frac{p}{m}}S.$$

we may write

$$E = \tfrac{1}{2}mV\sqrt{\frac{p}{m}}S = \pi mVS \times \frac{1}{2\pi}\sqrt{\frac{p}{m}}. \tag{40}$$

But $\dfrac{1}{2\pi}\sqrt{\dfrac{p}{m}}$ is the frequency ν. From (38), therefore, the total energy of a simple harmonic oscillator is always an integral multiple of the quantum of energy

$$E = nh\nu = n\epsilon. \tag{41}$$

The combined distribution law for the total energy, kinetic and potential, of a system of oscillators then takes the following form:

$$N_n = Ke^{-n\epsilon/kT}, \tag{42}$$

where N_n is the number of oscillators having exactly the energy $n\epsilon$. It should be noticed that the differential has disappeared and the distribution is now discontinuous. There are a number of oscillators with no energy, a number with one quantum each, a number with two quanta each and so on, but none with intermediate values.[1] For the total number of oscillators

$$N = \sum N_n = \sum Ke^{-n\epsilon/kT}, \tag{43}$$

where

$$\sum Ke^{-n\epsilon/kT} = K(1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + \cdots).$$

The total energy E of all the oscillators is given by the expression

$$E = \sum N_n n\epsilon = \sum Kn\epsilon e^{-n\epsilon/kT}. \tag{44}$$

Here

$$\sum Kn\epsilon e^{-n\epsilon/kT} = K\epsilon(e^{-\epsilon/kT} + 2e^{-2\epsilon/kT} + 3e^{-3\epsilon/kT} + \cdots).$$

If we divide (44) by (43) and multiply through by N, we obtain

$$E = \frac{N\epsilon\sum ne^{-n\epsilon/kT}}{\sum e^{-n\epsilon/kT}}. \tag{45}$$

This is a general expression for the total energy of any system of particles

[1] See Kunz, *Phil. Mag.*, **45**, 300 (1923).

which obey a "quantized" form of an exponential distribution law. We shall refer to it repeatedly. If we make the substitution,

$$X = e^{-\epsilon/kT},$$

simple algebraic division shows that

$$\sum ne^{-n\epsilon/kT} = \frac{e^{-\epsilon/kT}}{(1 - e^{-\epsilon/kT})^2}$$

and

$$\sum e^{-n\epsilon/kT} = \frac{1}{1 - e^{-\epsilon/kT}}.$$

Hence,

$$E = \frac{N\epsilon e^{-\epsilon/kT}}{(1 - e^{-\epsilon/kT})} = \frac{N\epsilon}{e^{\epsilon/kT} - 1} = \frac{Nh\nu}{e^{h\nu/kT} - 1}. \tag{46}$$

By differentiating with respect to the temperature, we obtain

$$\frac{dE}{dT} = Nk\left(\frac{\epsilon}{kT}\right)^2 \frac{e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2}.$$

Now, if the forces holding an atom in the lattice of a crystal are continuous, it can be shown mathematically that, for small displacements, the restoring force is proportional to the displacement.[1] Furthermore, the oscillations of an atom about its position in a lattice may be resolved into the three components and the atom treated as the equivalent of three simple harmonic oscillators. Thus, we see that, as an approximation, for the monatomic solids at low or moderate temperatures, when heated at constant volume,

$$C_v = \frac{dE}{dT} = 3Nk\left(\frac{\epsilon}{kT}\right)^2 \frac{e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2} = 3Nk\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}, \tag{47}$$

where

$$N = 6.061 \times 10^{23}, \qquad k = 1.372 \times 10^{-16} \text{ erg/deg.}$$

This is the Einstein formula for the heat capacity C_v of a monatomic solid. In Fig. 6 we have the Einstein curve compared with the characteristic experimental curve for monatomic solids. It will be seen that the two curves become asymptotic at high temperatures where both approach the value $3Nk = 3R = 5.96$ cals. We have here undoubtedly the true theoretical basis of the Dulong-Petit law. At lower temperatures, however, the Einstein curve falls with decreasing temperature more rapidly than the experimental curve. At a temperature where the Einstein equation gives a value of nearly zero for C_v, the substance still has a measurable heat capacity.

The explanation of this divergence appears to be simple enough. An inspection of equation (47) shows that the smaller the natural quantum for

[1] Jeans, *Theoretical Mechanics*, p. 348, Ginn & Co., New York, 1907.

the solid the higher the heat capacity at a given temperature, especially at low temperatures. But the quantum is proportional to the frequency

$$\epsilon = h\nu = h\frac{1}{2\pi}\sqrt{\frac{p}{m}}. \tag{48}$$

Now, if the two atoms should oscillate together as a unit and the constraints opposing the oscillation be something less than twice those acting on a single atom, we have the possibility of a smaller quantum. A number of atoms may pick up energy and vibrate as a single aggregate, the number being limited only by the size of the crystal. Of course, the larger the aggregates the fewer the number of them possible, so that the amount of energy taken up as "compound" quanta cannot be very large, but the divergence of the experimental equation is not very great. Furthermore, this divergence disappears at higher temperatures where the atoms are very largely "broken up" into single oscillators.

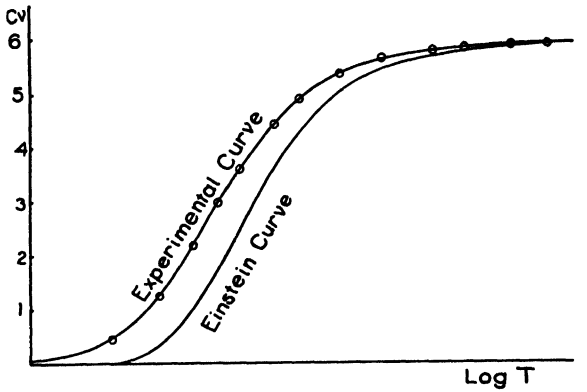


FIG. 6

The mathematical problem involved in the complete solution of the heat capacity curve for a monatomic solid is thus seen to be perfectly definite, but it is by no means easy of solution. In order to take account of the different frequencies, we shall have to write the Einstein equation in a generalized form

$$C_v = \sum N_i k \left(\frac{h\nu_i}{kT}\right)^2 \frac{e^{h\nu_i/kT}}{(e^{h\nu_i/kT} - 1)^2}, \tag{49}$$

where the summation is to be extended to all frequencies. Unfortunately, we have no means of calculating the number and magnitude of these various frequencies. Nernst and Lindemann [1] proposed a purely empirical equation

$$C_v = \frac{3R}{2}\left[\frac{\left(\frac{h\nu}{kT}\right)^2 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} + \frac{\left(\frac{h\nu}{2kT}\right)^2 e^{h\nu/2kT}}{(e^{h\nu/2kT} - 1)^2}\right]. \tag{50}$$

[1] *Z. Elektrochem.*, 17, 817 (1911).

This will be seen to represent C_v as $\frac{1}{2}$ the sum of the two "Einstein" terms with two frequencies, one twice the other. Fig. 7 shows the resultant curve obtained by plotting $\frac{1}{2}$ the sum of two such Einstein expressions. It is an approximation to the true heat capacity curve, as can be seen by comparison with Fig. 6.

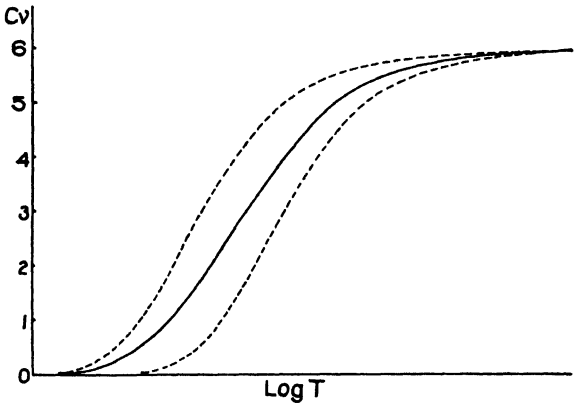


FIG. 7

The Debye Equation: Debye [1] has made the most satisfactory approach to a solution of the problem. In order to obtain an expression for the various frequencies in equation (48) above, he considers a monatomic solid as a homogeneous isotropic elastic medium, and assumes the heat energy to be present in the form of vibrations which range all the way from ordinary sound waves up to vibrations of a limiting frequency, ν_0, which presumably corresponds to the frequency of the individual atom ν that we have used in the Einstein equation. The total number of these vibrations is not infinite as is assumed in the ordinary theory of elasticity but is equal to $3N$, the number of degrees of freedom [2] of a solid body containing N atoms. From the theory of elasticity he gets an expression for the number of vibrations dz which lie between ν and $\nu + d\nu$,

$$dz = 9N \frac{\nu^2 d\nu}{\nu_0^3}.$$

If this value be substituted in (49) for N_i, the number of vibrations of a given frequency, and the summation changed to an integral, which is justifiable since the number of vibrations is large and they are continuously distributed over the range of frequencies, equation (49) becomes

$$C_v = \frac{9Nk}{\nu_0^3} \int_0^{\nu_0} \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \left(\frac{h\nu}{kT}\right)^2 \nu^2 d\nu, \qquad (51)$$

[1] *Ann. Physik.*, (4) **39**, 789 (1912).

[2] The concept of degrees of freedom will be discussed later.

where the integration is to be extended from 0 to the limiting frequency ν_0. When T is large, $\frac{h\nu}{kT}$ becomes small and the above expression reduces to a form which is readily integrable, giving a value

$$C_v = 3R,$$

as does the Einstein formula. When T is small, the expression can be integrated by expressing it as a series and the relation

$$C_v = aT^3 \tag{52}$$

is obtained. This relation is remarkably simple and is of great importance because it should hold for all solids whether monatomic or not, since, at low temperatures, the energy is found chiefly in the low frequency vibrations and the value of the limiting frequency is without significance. For intermediate values of T the values of C_v can only be obtained by a laborious process of calculation. It can be shown from equation (51), however, that C_v is the same function of $\frac{h\nu_0}{kT}$ for all monatomic substances and this function when plotted reproduces the experimental curve with great fidelity, as can be seen from Fig. 6, where the small circles represent the various points calculated from the Debye formula. In placing the Einstein and Debye curves on the diagram, it is assumed that ν_0 of the Debye formula is identical with ν of the Einstein formula. The two functions then approach each other asymptotically at high temperatures. Various investigators, including Kammerlingh Onnes,[1] have investigated specific heats at very low temperatures with especial care in order to test the relation

$$C_v = aT^3,$$

and have found it to be in very close agreement with experiment. It has been objected that the Debye assumption that the heat energy in a solid is distributed in an "acoustic spectrum" ranging from the longest sound waves up to the atomic vibrations themselves implies that heat should be conducted with the velocity of sound. The energy of the long waves is transferred with the velocity of sound but when the length of the wave is short enough to compare with the atomic distances, the analogy of a homogeneous medium is no longer correct. For instance, the propagation of ordinary sound waves in air can be satisfactorily calculated by assuming the air to be a continuous medium but if we were to deal with very high frequencies, we should have to recognize that air is made up of discrete particles.

Debye hoped to be able to calculate the specific heats of monatomic solids from their elastic constants since the frequencies of the vibrations which he postulates depend upon these quantities. The results obtained in this way, however, are not sufficiently accurate to be useful. Since the properties of matter assumed by Debye do not correspond exactly with reality and the

[1] Kammerlingh Onnes, *Comm. Phys. Lab.*, Leiden, No. 147 (1915).

final expression obtained is not readily usable, Debye's equation is not regarded as satisfactory by many, even though it agrees within the limits of experimental error with the data for monatomic solids.[1]

It must be recognized, however, that the remarkable success of Debye's equation in reproducing the experimental curve constitutes one of the outstanding triumphs of mathematical physics.

We shall return to a consideration of the Einstein formula. It has been said that this formula gives the heat capacity of an "ideal" solid. This is a contradiction in terms, however, for the word solid implies a rigid connection between one atom and another and the quantum theory tells us at once that the possibility exists of the atoms' oscillating as aggregates. Nevertheless, while the Einstein equation is an incomplete expression, it gives us a very good picture of the kinetic behavior of matter.

It has been noted that the fact that the heat capacity curves for monatomic substances can be superposed when plotted against log T indicates that the heat capacity is the same function of $\log\left(\frac{\theta}{T}\right)$ for all these substances. The Einstein equation fits this condition since it represents C_v as a function of $\frac{\epsilon}{kT}$. Here ϵ is the natural quantum for the atom and

$$\nu_0 = \frac{\epsilon}{h}$$

is the natural frequency of the atom oscillating in the crystal lattice. Attempts have been made to calculate these natural frequencies for substances from elastic properties, etc., but they have not been very successful. Only in the case of salts do we have a direct means of measuring ν_0, namely, the "residual ray" frequencies as measured by Rubens.[2] We shall make use of these later in calculating the entropies of the alkali halides. We can, however, draw inferences as to the comparative values of the fundamental frequency for different substances. We have the relation

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{p}{m}},$$

where p is the constraint on the atom and m its mass. The frequency should therefore be greater for hard substances of small atomic weight than for soft substances of high atomic weight. A comparison of lead and diamond shows this to be true. In comparing the heat capacity curves of different elements,

[1] Born and Karman (*Phys. Z.*, **13**, 297 (1912); **14**, 15, 65 (1913)) have derived an expression for heat capacity from a consideration of the properties of a crystal, the atoms of which are arranged in a lattice. They obtain an expression similar to Debye's but their derivation is too long and involved to be reproduced here.

[2] Rubens and Nichols, *Ann. Physik*, **60**, 418 (1897); Rubens and Aschkinass, *ibid.*, **65**, 241 (1898); Rubens, *ibid.*, **69**, 576 (1899); Rubens and Kurlbaum, *ibid.*, (4) **4**, 649 (1901); Rubens and Hollnagel, *Phil. Mag.*, (6) **19**, 761 (1910).

it is convenient to make use of the characteristic constant θ. We may arbitrarily define this constant as the temperature at which

$$C_v = 2.98 \text{ cal.},$$

since this temperature corresponds to the steepest part of the curve and may be readily located graphically. For this value of θ from the Einstein equation,

$$\frac{h\nu_0}{kT} = 2.98;$$

hence

$$\frac{h\nu_0}{k \times 2.98} = \theta. \tag{53}$$

The smaller the value of θ and hence of ν_0, the higher the heat capacity at a given temperature.

Heat Capacity Curves of Irregular Types: As has been remarked, for high temperatures the Einstein formula approaches the limiting value

$$3R = 5.96 \text{ cal.}$$

While the characteristic curve for monatomic solids appears to approach this value at ordinary temperatures, in the case of some of the metals the value of C_v rises above this limit at high temperatures and in the case of the alkali metals this limit is exceeded at low temperatures. It has been suggested [1] that the high heat capacity is due to the electrons of the metal taking up kinetic energy and behaving as the heavier atoms. Lewis [2] has suggested this explanation for the case of the alkali metals. That the electrons do behave in this manner seems highly plausible. J. J. Thomson [3] has suggested that at ordinary temperatures the electrons of a metal form a lattice just as do the atoms in the crystal and that their behavior toward heat energy is the same as that of the atoms at very low temperatures where the T^3 law applies. If this be true, as the temperature is raised, the electron groups are broken up into smaller and smaller aggregates and have an increasingly greater heat capacity. Likewise, in the case of the alkali metals where the constraints on the electrons are small, we should expect from equation (48) that the quantum for the individual electron would not be very great even though the

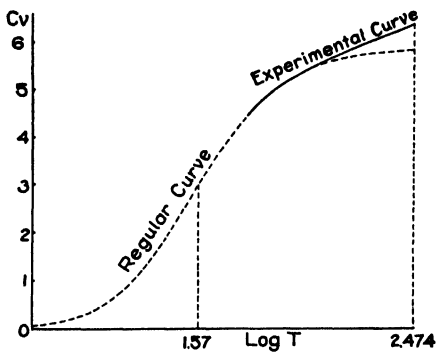


FIG. 8

[1] J. Koenigsberger, *Z. Elektrochem.*, 17, 289 (1911).

[2] Lewis, Eastman, and Rodebush, *Proc. Nat. Acad. Sci.*, 4, 25 (1918).

[3] *Phil. Mag.*, 44, 657 (1922).

mass of the electron is a small fraction of the mass of an atom. It must not be overlooked, however, that abnormally high values of C_v appear only as we approach the melting point, where large amplitudes of vibrations of the atoms are to be expected. While, at ordinary temperatures, potassium is undoubtedly a crystalline substance, it gives no X-ray pattern,[1] behaving in this respect as though it were amorphous. At lower temperatures, a definite X-ray pattern is obtained. This would seem to be proof of very large amplitudes of vibration for the atoms. The low values of ν_0 for the alkali metals must be due to the weakness of the forces between atoms. The assumption of simple harmonic oscillation can only be made for small amplitudes. The application of quantum theory to inharmonic [2] oscillations is still uncertain but it seems probable that an additional quantum of energy may be required when this oscillation becomes inharmonic. Abnormally high values of C_v are probably not due entirely to the electron.

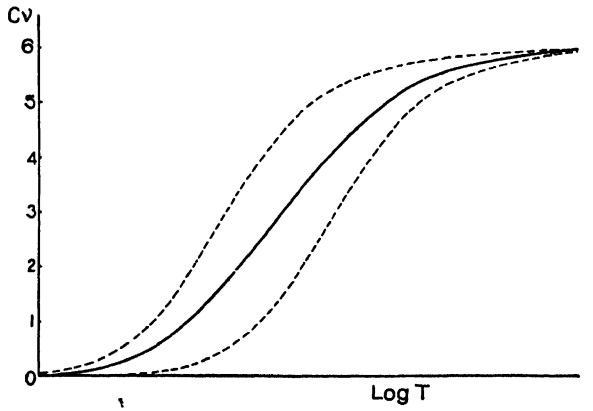


FIG. 9

The heat capacity curves for the compounds are, with a few exceptions, less steep than the characteristic curve of the elements. This is what we should expect if the heat capacity of the compound is the sum of the heat capacities of its elements, each variety of atom having its own quantum. Fig. 9 shows the form of a curve in which

$$C_v = \tfrac{1}{2}(C_{v_1} + C_{v_2}),$$

where C_{v_1} and C_{v_2} are the heat capacities of two elements having widely different values of θ. In a substance like crystalline potassium chloride which is essentially monatomic, with atoms of not greatly different masses, subject to similar constraints, we find the curve of C_v for $\frac{1}{2}$ gram mol. is of practically the same form as the regular curve, since the quanta for the potassium and

[1] McKeehan, *Proc. Nat. Acad. Sci.*, **8**, 254 (1922).

[2] See Kratzer, *Z Physik*, **3**, 289 (1920).

chlorine atoms are nearly equal. This directs our attention to the fact that an absolutely "regular" curve for the heat capacity of a monatomic solid is only to be expected from an element which is not made up of isotopes.

The case of graphite is of interest. Graphite is undoubtedly a monatomic solid, yet the curve is much flatter than the regular curve. This would indicate the existence of more than one fundamental frequency and the crystal structure as determined by X-ray methods bears this out. The X-ray pattern [1] indicates that the carbon atom in graphite is attached very firmly to three other atoms and loosely to a fourth. We shall refer to this again in connection with the relative stability of graphite and diamond.

At low temperatures, the C_v curve for a few compounds such as carborundum and magnesium oxide is steeper than the regular curve of the elements and has about the same slope as the curve for the Einstein equation. Nernst [2] has pointed out that these are high melting substances and suggests the possibility that here we have, inside the molecules, atoms under comparatively weak constraints which are, so to speak, insulated from the rest of the solid by the very stiff linkage between molecules. Under these circumstances the isolated atoms become "ideal" oscillators and their heat capacity is given by the Einstein equation. This is an interesting suggestion but it is evidently one which must be verified by crystal structure.

The Empirical Calculation of Entropy by the Third Law

Monatomic Solids: In Fig. 6 we have plotted the Einstein and Debye formulas, assuming that the limiting frequency ν_0 is the same for both expressions. The Debye equation corresponds so closely to the experimental data that for practical purposes of calculation we may assume it to be exact. By the third law, the entropy of a crystalline solid at 298° K. is given by the integral

$$S_{298} = \int_0^{298} C_p d\ln T = 2.3 \int_0^{298} C_v d \log T + 2.3 \int_0^{298} (C_p - C_v) d \log T. \quad (54)$$

The term $\int_0^T C_v d \log T$ corresponds to the area under the Debye curve, Fig. 6, up to the limiting ordinate log 298 and may be evaluated graphically when we know θ. Since we cannot integrate the Debye expression except at high temperatures, we can obtain no general expression for S_{298} but must perform repeated graphic integrations. On the other hand, the Einstein expression for

$$\int_0^T C_v d \log T$$

[1] Debye and Scherrer, *Phys. Z.*, **18**, 291 (1917). Hull, *Phys. Rev.*, **10**, 661 (1917).

[2] Nernst, *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes*, Halle, 1918.

is readily integrated. Furthermore, it may be noted that the difference in

$$2.3\int_0^{298} C_v d\log T$$

for the Einstein and Debye expressions is equal to the area between the two curves and is the same for all substances. We shall show later that this area is equal to R for substances whose heat capacities approach the Dulong-Petit value.

The last term of (54) by substitution from (32) becomes

$$\tfrac{2}{3}(C_{p_{298}} - C_{v_{298}}).$$

For the Einstein expression we obtain the integral

$$\int_0^T C_v d\ln T = 3R\int_0^T \frac{e^{h\nu_0/kT}\left(\frac{h\nu_0}{kT}\right)^2}{(e^{h\nu_0/kT}-1)^2} d\ln T$$
$$= 3R\left[\frac{\frac{h\nu_0}{kT}}{e^{h\nu_0/kT}-1} - \ln(1-e^{-h\nu_0/kT})\right], \tag{55}$$

where the value of ν_0 is to be determined from the heat capacity data. We have defined θ as the temperature where

$$C_v = \tfrac{3}{2}R.$$

By (53), θ_E for the Einstein equation $= \dfrac{h\nu_0}{2.98k}$. For the Debye formula

$$\theta_D = \frac{h\nu_0}{4.02k}.$$

Since the Debye equation agrees with the experimental data, we then have

$$\theta_E = 1.35\theta_D = 1.35\theta_{\text{experimental}}.$$

If the upper limit of integration in (55) is 298° K., equation (54) becomes

$$S_{298} = 5.96\left[\frac{0.0135\theta}{e^{0.0135\theta}-1} - \ln(1-e^{-0.0135\theta})\right] + 1.99 + \tfrac{2}{3}(C_{p_{298}} - C_{v_{298}}), \tag{56}$$

where θ is the temperature at which the experimental value for C_v is equal to $\frac{3}{2}R$. For those substances whose specific heats approach the Dulong-Petit value this expression gives the entropy within the limits of experimental error.

We have already mentioned that in the case of the alkali halides we have a direct means of determining ν_0. Strictly speaking, a salt such as potassium chloride cannot be regarded as a monatomic crystal even though the unit in the lattice is a single atom, because it is made up of two different kinds of atoms of different masses, and hence, presumably, of different frequencies. The con-

straints may reasonably be supposed to be the same for both atoms. As a matter of fact, however, the experimental data for the heat capacity per $\frac{1}{2}$ gram mol. for these salts fits remarkably well the characteristic curve for monatomic solids. Furthermore, the work of Rubens and Hollnagel [1] shows that the infra-red resonance spectrum is simple. If we calculate ν_0 from the mean wave length λ_0 as determined by Rubens and Hollnagel and substitute the corresponding value of θ in equation (56), we get remarkable agreement with the entropies calculated from heat capacity data. The results are given in Table II.

TABLE II

ENTROPIES OF ALKALI HALIDES CALCULATED FROM RESIDUAL RAY FREQUENCIES

Entropy per $\frac{1}{2}$ gram mol.

	$\lambda_0(\mu)$	ν_0	Calculated	Experimental
NaCl.....	51.7	5.81×10^{12}	8.72	8.72
KCl.....	63.4	4.73×10^{12}	9.89	9.86
KBr.....	82.3	3.65×10^{12}	11.40	11.21

There can be little doubt as to the real significance of ν_0 as measured by residual ray frequencies.

THE RELATION BETWEEN ENTROPY, FREQUENCY AND ATOMIC WEIGHT FOR SOLIDS

The Debye equation (51) may be integrated with respect to $dlnT$,

$$\int_0^T C_v dlnT = \frac{9Nk}{\nu_0^3} \int_0^T \int_0^{\nu_0} \frac{e^{h\nu/kT} \left(\frac{h\nu}{kT}\right)^2}{(e^{h\nu/kT} - 1)^2} \nu^2 d\nu dlnT$$

$$= \frac{9Nk}{\nu_0^3} \int_0^{\nu_0} \left[\frac{\frac{h\nu}{kT}}{e^{h\nu/kT} - 1} - ln(1 - e^{-h\nu/hT}) \right] \nu^2 d\nu.$$

At high temperatures, the right-hand side of the above equation may be simplified and integrated with respect to $d\nu$,

$$\frac{9Nk}{\nu_0^3} \int_0^{\nu_0} \left(1 - ln\frac{h\nu}{kT}\right) \nu^2 d\nu = 3R \left(\frac{4}{3} + ln\frac{kT}{h\nu_0}\right). \quad (57)$$

The integrated Einstein expression (55) at high temperatures becomes

$$3R \left(1 + ln\frac{kT}{h\nu_0}\right).$$

[1] *Sitzb. preuss. Akad.*, 52 (1910). *Phil. Mag.*, (6) **19**, 761 (1910).

[2] See Planck, Wärmestrahlung, 4th edition, p. 214, Barth, Leipzig, 1921.

The two expressions thus differ by R and this fact is used in setting up the empirical equation for entropy (56). The Debye equation can only be integrated at high temperatures, so the Einstein equation, which is already simple, is used in the integral of (56). On the other hand, the difference between the Debye and Einstein integrals does not differ appreciably (i.e., by an amount greater than the experimental error) from R so long as $C_v > 5.5$ calories.

For large values of T (i.e., when $C_v = 3R$), we have from (56) and (57)

$$S_T = 3Rln\frac{kT}{h\nu_0} + \tfrac{2}{3}(C_{p_T} - C_{v_T}) + 4R.$$

But from (48)

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{p}{m}} \qquad \text{and} \qquad m = \frac{M}{N},$$

where M is the atomic weight and N Avogadro's number. Hence we may write

$$S_T = \tfrac{3}{2}Rln\frac{M}{p} + 3RlnT + \tfrac{2}{3}(C_{p_T} - C_{v_T}) + C. \tag{58}$$

At a given temperature of comparison for a type of substances where the constraints do not differ greatly, the $(C_p - C_v)$ term will be about the same for each substance and equation (58) may be written

$$S_T = \tfrac{3}{2}RlnM + C. \tag{59}$$

This relation has been shown by Latimer [1] to hold with accuracy at 298° K. for 16 binary salts for which C_v approaches the Dulong-Petit value closely.

If we wish to compare the entropies of the metals at a given temperature, we find that the constraints vary so widely that it is necessary to take them into account. The constraints may be calculated approximately from the elastic constants and Eastman [2] has recently shown that the entropies of the metals at 298° K. may be represented satisfactorily by an equation of the form

$$S = \tfrac{3}{2}RlnM + Rln\frac{\beta^{3/2}}{V} + C, \tag{60}$$

where V is the atomic volume and β the compressibility.

In the case of substances other than monatomic solids where the heat capacity curve cannot be represented by an equation, it is necessary to plot C_p against log T and resort to graphic methods of integration to obtain the entropies. Since log T becomes infinite as T approaches zero, the method of graphical integration must be supplemented at low temperatures by another method. At these temperatures we have the T^3 relation from which it is

[1] *J. Am. Chem. Soc.*, **43**, 818 (1921).
[2] *J. Am. Chem. Soc.*, **45**, 80 (1923).

easy to show that the entropy below any given low temperature is given by the equation

$$S = \tfrac{1}{3}aT^3. \tag{61}$$

The T^3 relation holds with an accuracy of 1 per cent up to temperatures where

$$C_v = 0.2 \text{ cal.}$$

For a substance that is a liquid at 298° K., it is necessary to include the entropy of fusion, or, if a gas, the entropy of fusion and vaporization, as well as the integral

$$\int_0^T C_p d\ln T$$

from 0° K. in the value for S_{298}. For liquids we neither have sufficient experimental data nor a satisfactory theory from which to attempt generalizations in regard to heat capacity or entropy.

Table III is a table of atomic entropies as compiled (1922) by Lewis, Gibson, and Latimer.[1]

Conventional Chemical Constants: We are now in a position to criticize the "conventional chemical constant" calculated from equation (24), using Nernst's empirical extrapolation for heat capacity. As a vapor pressure equation it will be quite satisfactory, since, in the region where the vapor pressure is measurable, the heat capacity can be adequately represented by an equation in powers of T. In order to make use of the third law for calculation of equilibrium constants, however, it is necessary to extrapolate to 0° K. From Fig. 4 we see that while the atomic heat capacities in general approach each other at ordinary temperatures and at 0° K., in the interval between these two temperatures ΔC_p is a quantity which may vary from zero to a considerable magnitude. This causes serious errors not so much in the integral

$$\int_0^T \Delta C_p dT$$

as in the integral

$$\int_0^T \frac{\Delta C_p dT}{T}$$

at low temperatures. All this, of course, is in addition to the question of the application of the third law to liquids. The conventional chemical constant then can be relied upon to give scarcely more than a qualitative measure of the reaction tendencies and is to be regarded as an approximation of the same sort as Berthelot's principle of equating the free energy to the total energy.

[1] *J. Am. Chem. Soc.*, **44**, 1008 (1922).

TABLE III

ATOMIC ENTROPIES AT ONE ATMOSPHERE AND 298° K.

Electricity (E-, g)	3.28	Chlorine ($\frac{1}{2}Cl_2$, g)	26.3
Hydrogen ($\frac{1}{2}H_2$)	14.72	Chlorine (Cl, g)	36.35
Hydrogen (H)	25.72	Argon	36.70
Helium	29.83	Potassium	16.6
Lithium	7.6	Potassium (g)	36.63
Lithium (g)	31.48	Calcium	10.64
Beryllium	7.3	Calcium (g)	36.71
Carbon (diamond)	0.6	Titanium	6.6
Carbon (graphite)	1.3	Chromium	5.8
Nitrogen ($\frac{1}{2}N_2$)	22.8	Manganese	7.3
Nitrogen (N)	33.57	Iron	6.71
Oxygen ($\frac{1}{2}O_2$)	24.0	Cobalt	7.2
Oxygen (O)	33.97	Nickel	7.2
Fluorine (F)	34.48	Copper	8.18
Neon	34.66	Zinc	9.83
Sodium	12.2	Zinc (g)	38.17
Sodium (g)	35.06	Bromine ($\frac{1}{2}Br_2$, l)	16.3
Magnesium	8.3	Bromine ($\frac{1}{2}Br_2$, g)	27.7
Aluminum	6.82	Bromine (Br, g)	38.77
Silicon (metal)	4.7	Krypton	38.88
Phosphorus (P, g)	35.95	Rubidium (g)	38.97
Sulfur (rhombic)	7.6	Zirconium	9.5
Sulfur (monoclinic)	7.8	Molybdenum	7.5
Sulfur (S, g)	36.04	Ruthenium	6.9
Rhodium	7.6	Cerium	13.8
Palladium	8.9	Tungsten	8.4
Silver	10.25	Osmium	7.8
Cadmium	11.80	Iridium	8.7
Cadmium(g)	39.79	Platinum	10.0
Tin (white)	11.17	Gold	11.0
Tin (gray)	9.23	Mercury (l)	17.8
Iodine ($\frac{1}{2}I_2$, s)	13.3	Mercury (g)	41.51
Iodine ($\frac{1}{2}I_2$, g)	30.9	Thallium	14.6
Iodine (I, g)	40.15	Lead	15.53
Xenon	40.23	Niton	41.81
Cesium (g)	40.28	Thorium	13.6
Lanthanum	13.7	Uranium	11.1

The advantage which the Nernst approximation formula possesses over the Berthelot principle as a qualitative measure of the reaction tendencies is best exemplified in the case of reactions with similar heats of reaction but with different volume changes. An example in heterogeneous equilibria will best illustrate this advantage.

As was pointed out originally by Thomsen,[1] the nitrates, although possessing a considerably greater heat of formation than the corresponding carbonates, are much more readily decomposed. Here actually was a remarkable exception to the Berthelot principle, the explanation of which was impossible to the adherents to the principle. Application of the Nernst approximation formula gives, however, an indication of the reason for the discrepancy.

The formation of a nitrate may be generalized by means of the equation

$$2MO + 4NO_2 + O_2 = 2M(NO_3)_2 + 2Q, \qquad (1)$$

[1] Thermochemische Untersuchungen, Vol. 3, p. 555.

in which M denotes a diatomic metal, Q ($= -\Delta H$) is the heat of formation of 1 mol. of nitrate from oxide, nitrogen dioxide and oxygen. For complete dissociation of the gaseous products into nitric oxide and oxygen, the equation becomes

$$2MO + 4NO + 3O_2 = 2M(NO_3)_2 + 2Q'. \tag{2}$$

The Nernst approximation formula for such heterogeneous reactions has the general form

$$\log K_p = -\frac{Q}{4.571T} + \Sigma n.1.75 \log T + \Sigma nC, \tag{3}$$

where K_p refers to the equilibrium constant expressed as partial pressures of the gaseous *reactants* in atm. divided by the partial pressures of the gaseous *resultants* in atm., Σn represents the change in the number of gaseous molecules (reactants − resultants), ΣnC represents the algebraic summation (reactants − resultants) of the conventional chemical constants of the participating gases each multiplied by its molecular coefficient in the reaction equation. Thus, in Equation (1) above, $\Sigma n = 5$; in Equation (2), $\Sigma n = 7$. Assuming that the conventional chemical constant for O_2 is 2.8, for NO_2, 3.3 and for NO, 3.5,[1] the corresponding value for ΣnC in Equation (1) is

$$\Sigma nC = 4(3.3) + 2.8 = 16$$

and in Equation (2)

$$\Sigma nC = 4(3.5) + 3(2.8) = 22.4.$$

The equilibrium equations become respectively

$$\log p_{NO_2}{}^4 p_{O_2} = -\frac{2Q}{4.571T} + 8.75 \log T + 16 \tag{1a}$$

and

$$\log p_{NO}{}^4 p_{O_2}{}^3 = -\frac{2Q'}{4.571T} + 12.25 \log T + 22.4. \tag{2a}$$

If the total gas pressure be P, it is obvious that, in Equation (1),

$$p_{NO_2} = \tfrac{4}{5}P \quad \text{and} \quad p_{O_2} = \tfrac{1}{5}P,$$

provided the pure nitrate be employed. Similarly, in Equation (2),

$$p_{NO} = \tfrac{4}{7}P \quad \text{and} \quad p_{O_2} = \tfrac{3}{7}P.$$

For the temperatures, T_1 and T_1', at which dissociation reaches atmospheric pressure, in the two cases, namely, $P = 1$, it is evident that the equations become respectively:

$$\log \frac{4^4}{5^5} = -\frac{2Q}{4.57T_1} + 8.75 \log T_1 + 16 \tag{1b}$$

and

$$\log \frac{4^4 \times 3^3}{7^7} = -\frac{2Q'}{4.57T_1'} + 12.25 \log T_1' + 22.4 \tag{2b}$$

or

$$\frac{Q}{4.571T_1} = 4.4 \log T_1 + 8.5 \tag{1c}$$

and

$$\frac{Q'}{4.571T_1'} = 6.1 \log T_1' + 11.4. \tag{2c}$$

[1] Nernst, *Theoretical Chemistry*, 8–10th Edition, Book IV, Chap. V. *Die Theoretischem und Experimentellen Grundlagen des Neuen Wärmesatzes*, p. 112, Halle (1918).

In the corresponding case of the dissociation of a carbonate of a divalent metal

$$MO + CO_2 = MCO_3 + Q'',$$

it follows, from analogous treatment, that

$$\log K_p = \log p_{CO_2} = -\frac{Q''}{4.57T} + 1.75 \log T + 3.2, \tag{4}$$

where $n = 1$ and the conventional chemical constant for CO_2 is 3.2.[1]

For the temperature T''' at which the pressure of carbon dioxide reaches 1 atm., the equation becomes, therefore,

$$\frac{Q''}{4.57T'''} = 1.75 \log T''' + 3.2. \tag{4c}$$

Comparison of equations (1c) and (2c) with that of (4c) shows obviously that when the respective values of Q for the two dissociations are the same, the nitrate must dissociate at a considerably lower temperature than the carbonate. Berthelot's principle would demand equal dissociation temperatures. It is evident, therefore, that the Nernst approximation formula is a much better basis for estimating qualitatively the reaction tendency in any equilibrium process than is the Berthelot principle. This is generally true, not only with heterogeneous reactions, but also with homogeneous gas reactions.

Rolla [2] has studied the dissociation of cupric nitrate and has applied the Nernst approximation formula with good concordance to the equilibrium data, on the lines of the above treatment. The dissociations of metal chloride-ammonia compounds are good examples also of the applicability of the Nernst approximation formula, since as is evident from the formulæ, $2AgCl.3NH_3$, $LiCl.2NH_3$, $PdCl_2.4NH_3$, $CaCl_2.4NH_3$, $CaCl_2.6NH_3$, $ZnCl_2.6NH_3$, varying values of Σn will be found in the $\log T$ term. Bodenstein [3] has indicated another such case. The reduction of zinc oxide by carbon occurs at about the same temperatures as the reduction of potassium carbonate by carbon, although, in the latter case, much more heat is absorbed. The approximation formula takes count of this in the greater number of gas molecules involved,

$$ZnO + C = Zn + CO,$$

$$K_2CO_3 + 2C = K_2 + 3CO.$$

The same divergence between the Berthelot principle and the Nernst approximation formula is evident in homogeneous gas reactions involving dissociation of a gas into several reaction products. The application of the approximation formula to a number of such dissociations has been made by Brill [4] and Pollitzer,[5] cited by Nernst [6] in his review of the heat theorem. The following table gives the observed temperature at which dissociation is one-half complete in a series of reactions, together with the heat of the reaction, $Q\ (= -\Delta H)$, the working pressure P and the temperature calculated for one-half dissociation on the basis of the approximation formula, where

$$\log K_p = \log \frac{x^2}{1-x} = -\frac{Q}{4.57T} + 1.75 \log T + 3,$$

whence, for $x = 0.5$,

$$T = \frac{Q}{4.57(\log 2 + 1.75 \log T + 3 - \log P)}.$$

[1] Nernst, *loc. cit.*

[2] *Gazz. chim. ital.*, **45**, I, 444 (1915).

[3] *Z. Elektrochem.*, **23**, 103 (1917). Cf. Nernst, *loc. cit.*, p. 124.

[4] *Z. physik. Chem.*, **57**, 735 (1907).

[5] Monograph *Ahrens Sammlung*, Vol. 17, 1912.

[6] *Loc. cit.*, p. 121.

TABLE V

GAS DISSOCIATIONS

Reaction	Q	P	$T_{obs.}$	$T_{calc.}$
$2NO_2 = N_2O_4$	12,450	0.65	323° K.	340° K.
$2HCOOH = (HCOOH)_2$	14,780	1	410	410
$2CH_3COOH = (CH_3COOH)_2$	16,600	1	425	450
$PCl_3 + Cl_2 = PCl_5$	18,500	1	480	500
$HBr + C_5H_{10} = C_5H_{11}Br$	19,400	1	483	525
$HBr + C_5H_{10} = C_5H_{11}Br$	19,400	0.1	462	470
$H_2O + SO_3 = H_2SO_4$	21,850	1	623	599

It will be noted that, in these cases, there is, in accord with the Berthelot principle, also a rough proportionality between Q and T. When, however, the dissociation yields more than two resultant molecules, this proportionality does not apply as is evident in the case of the dissociation of hexahydrobenzene to benzene and hydrogen,

$$C_6H_6 + 3H_2 = C_6H_{12}.$$

Four molecules of dissociated products are obtained. The heat of dissociation is approximately 43,000 calories. In spite of this high heat of reaction, hexahydrobenzene may be dehydrogenated at 300° C., and even in presence of excess hydrogen thirty per cent decomposition occurs at 400° C.[1] This is a much lower temperature than would be expected on Berthelot's principle from the preceding cases of dissociation. That the Nernst approximation formula is applicable to this reaction is evident from the calculation of Pease given by Dougherty and Taylor,[2] where the formula

$$\log K_p = -\frac{43{,}400}{4.57T} + 3(1.75 \log T) + 3(1.6)$$

gives the following values for $\log K_p$:

T° C.	0	27	200	227	527
$\log K_p$	− 16.91	− 13.85	− 1.21	− 0.03	+ 8.17

These values are in evident agreement with the catalytic observations that the reaction changes from hydrogenation to dehydrogenation in the temperature interval 180°–300° C.

STABILITY OF SUBSTANCES AT HIGH TEMPERATURES

A common generalization is that compounds formed from their elements with the absorption of heat are stable at high temperatures. The third law together with the quantum theory of specific heats enables us to discuss this question with considerable assurance. van't Hoff[3] anticipated some of our conclusions in 1904 when he stated that if two forms of a substance exist, the

[1] Sabatier and Gaudion, *Compt. rend.*, **168**, 670 (1919).

[2] *J. Phys. Chem.*, **27**, 535 (1923).

[3] van't Hoff, Boltzmann Festschrift, p. 233, Barth, Leipzig, 1904. This conclusion assumes that the specific heat curves do not cross.

one with the higher specific heat will be stable at high temperatures. The question is worthy of consideration in some detail. Let us consider first the reaction

$$A \rightleftharpoons B,$$

where A and B are two different crystalline forms of the same substance. We have the equation (4)

$$\Delta F = \Delta H - T\Delta S = \Delta H_0 + \int_0^T \Delta C_p dT - T\int_0^T \frac{\Delta C_p dT}{T},$$

where ΔF is the increase in free energy in passing from A to B. The form with the lesser free energy will, of course, be the more stable and, at 0° K., this will be the form with the lesser total energy content. As we raise the temperature, ΔH will change by the integral

$$\int_0^T \Delta C_p dT.$$

ΔF will be changed by the difference

$$\int_0^T \Delta C_p dT - T\int_0^T \frac{\Delta C_p dT}{T}.$$

Since the second integral must, in general, be greater than the first (on account of the factor T in front of the sign), ΔF must always diverge from ΔH, i.e., increase if ΔH decreases, so long as the sign of ΔC_p remains unchanged with increasing temperature.

The form more stable at 0° K. must have the stronger constraint acting in the crystal lattice and if the unit in the crystal lattice is the same in both forms (i.e., of the same mass), then the Einstein equation tells us that the less stable form has the higher heat capacity over the lower temperature ranges at least.

In terms of the above equation, suppose that A is the stable form at 0° K., then ΔF is positive, likewise ΔC_p. As we raise the temperature, ΔH increases slowly with the temperature but the term

$$T\int_0^T \frac{\Delta C_p dT}{T}$$

increases more rapidly. At high temperatures, ΔC_p approaches zero, for monatomic substances at least, while the term

$$T\int_0^T \frac{\Delta C_p dT}{T}$$

continues to increase with the temperature so that at some temperature it is highly probable that ΔF will change sign. Here we will have a transition point and above this temperature phase B becomes stable. The transition temperature might, of course, be above the melting point.

This is the general behavior to be expected for a case as above, but if the substance contain complex molecules, these may be of different structure in the different crystal forms and we can no longer make any predictions about the trend of the specific heat curves. The curves for the two modifications might even cross. For the simple case which we have assumed, however, the conclusions appear quite sound. Rhombic and monoclinic sulfur seem to be an illustration of such behavior, although their heat capacity curves are not regular.

The case of graphite and diamond appears to be at first sight an exception. At all temperatures graphite is the more stable substance and yet it has the higher specific heat at all temperatures. Furthermore, its heat capacity curve is less steep than the regular curve, although it is undoubtedly monatomic. The crystal structure (see p. 1156) appears to explain the situation. The atom of carbon in graphite is constrained in a plane with forces which are greater than in the diamond lattice. At right angles to the plane the forces are very weak and we may suggest that the heat capacity lies almost entirely in the oscillations normal to the plane of the crystal. This would explain its anomalous heat capacity.

For a more complex reaction such as the formation of a compound from its elements, we can make no *a priori* deductions as to the sign of ΔC_p. We have seen that so long as ΔC_p does not change sign, ΔF and ΔH must diverge as the temperature is increased. If a compound is unstable at low temperatures, the free energy of formation from its elements then will be positive and at 0° K. will be equal to the heat of formation. If ΔC_p of formation be negative, then, at higher temperatures, ΔF must remain positive and the compound will continue unstable. If ΔC_p is positive, ΔF may become negative and the compound become stable at temperatures sufficiently high. In the average case, however, what we may expect to happen is that some new dissociation reaction may set in to destroy our compound. For example, let us consider the formation of ozone

$$\tfrac{3}{2}O_2 \rightarrow O_3.$$

At low temperatures, ΔF and ΔH for this reaction are positive. ΔC_p is probably negative and we can expect no increased percentage of ozone present at equilibrium at higher temperatures. If ΔC_p were positive, we should probably be defeated in our attempt to convert ozone to oxygen at high temperatures by the dissociation of ozone into monatomic oxygen, an entirely different reaction. The same considerations apply to compounds stable at low temperatures. If ΔC_p be positive, stability will persist at high temperatures until some dissociation reaction intervenes.

The third law tells us that endothermic compounds are unstable at low temperatures but the common belief that endothermic compounds are stable at high temperatures is scarcely more than a superstition. The important factor is ΔC_p of formation and, even if it be positive, the compound will probably cease to be stable due to other reactions. In the sun, for instance, not

only do molecules dissociate into atoms but atoms dissociate into electrons. Our generalizations in regard to specific heats assume that they approach the Dulong-Petit value as a limit at high temperatures, but this is only true for a short temperature interval. At still higher temperatures the amplitudes of vibration of the atoms become so great that the motion ceases to be simple harmonic and dissociation analogous to evaporation begins to take place. The hope of synthesizing substances which are unstable at low temperatures by going to higher temperatures is therefore illusory in the sense that no large yields are to be expected. High temperature, of course, favors the attainment of equilibrium and small amounts of a substance may be present at equilibrium even if its free energy of formation is a large positive quantity.[1]

The Equipartition of Energy

In the derivation of the Einstein expression for heat capacity we made use of the distribution laws (34) and (35) for the kinetic and potential energies respectively of a system of oscillators, promising the reader that we would discuss the theoretical basis of these equations later. These equations are special cases of a general theorem of molecular mechanics, as is also Maxwell's law for the distribution of the velocities of gas molecules. This very fundamental theorem is commonly known as the *Principle of the Equipartition of Energy.* This important principle, which is a deduction from the laws of classical mechanics, seems to lead to results so at variance with the facts, except in the case of the monatomic gases, that for many years it has been regarded as of doubtful validity. The recent introduction of the quantum theory, however, bids fair not to invalidate this principle but to explain its apparent failure. It is therefore a concept with which every student of physical chemistry should be familiar. The principle of equipartition is one of the important deductions of what is known as statistical mechanics. Maxwell[2] and Boltzmann[3] were the most prominent of the earlier workers in this field. Willard Gibbs,[4] however, has become the most renowned because of the

[1] Since

$$\ln K_p = -\frac{\Delta F}{RT},$$

it follows that at temperatures sufficiently high K_p approaches unity and all the substances involved in the reaction will be present in considerable amounts. Unless ΔF be small, however, the temperature must be very high to produce this effect. For the formation of NO from N_2 and O_2 Lewis and Randall (Thermodynamics, p. 560, McGraw-Hill Co., New York, 1923) have calculated the equation

$$\Delta F = 21{,}500 - 2.5T.$$

Here both the sign of ΔC_p at low temperatures and the small value of ΔF combine to favor the yield of NO at high temperatures.

[2] *Collected Works*, II, p. 713.

[3] *Sitzb. kgl. Akad. Wiss., Wien*, LVIII.

[4] Elementary Principles in Statistical Mechanics, Yale University Press, New Haven, 1914.

simplicity and elegance of his mathematical treatment of the subject. Unfortunately, Gibbs' treatment is so wanting in concrete illustrations and in the approaches which must be built from the more familiar modes of reasoning to a method that is new and abstract that the reader [1] who is unfamiliar with the subject has difficulty in finding out what Gibbs had in mind. Jeans in his Dynamical Theory of Gases [2] has treated the Principle of Equipartition exhaustively and with mathematical rigor (in so far as the treatment can be made rigorous) but his treatment is laborious to the reader who is not inclined strongly toward mathematics. The reader, however, will find it profitable to read Jeans in order to get a clear idea of the concepts with which we shall be dealing. We shall try to sketch for the reader briefly and concretely the method of reasoning used by Gibbs.

Concept of Generalized Space: Suppose we wish to study the behavior of a monatomic gas whose molecules are assumed to be dimensionless points, i.e., incapable of acquiring a rotational momentum. The reader is familiar with the methods of analytical geometry by which the position of a single molecule may be indicated by a point in a system of three rectangular coördinate axes. One must be careful not to confuse the point with the molecule itself. The molecule may be sealed up in a glass tube while the point and coördinate axes are chalk marks on a blackboard. In a similar manner, if we lay off another system of three axes each of which represents momentum in a direction corresponding to one of the axes of the first system, then a second point will specify completely the momentum of the molecule. When position and momentum are completely specified, then the total energy of the molecule is determined: that part of the energy that is due to position being called potential energy, and that part that is due to momentum, kinetic energy.

Now if we could draw a six-dimensional set of coördinates on the blackboard, we should be able to represent the location and momentum of our molecule by a single point. We cannot do this but as a matter of fact we cannot draw to scale a three-dimensional space on the blackboard. What we do is to draw two-dimensional cross sections of the three-dimensional space. We can do the same for the six-dimensional space. Analytically there is no difficulty. The equation for a spherical surface in six dimensions resembles the equation for a spherical surface in three dimensions except that it has more terms. The concept of higher dimensional space offers no difficulties mathematically and it is of great usefulness in the study of matter which is made up of enormous numbers of molecules. Many of the obscure analytical relations involving energy simply become theorems in geometry or hydrodynamics. Thus, if we combine two six-dimensional systems, we can completely specify the condition of two molecules by a single point and if we have a quantity of gas containing N molecules, then a single point in a $6N$ dimensional set of coördinate axes will at any instant specify completely the position

[1] Part of the difficulty is due to the order of presentation. It is recommended that the student read Chaps. I, IV, V, VI, and VII of Gibbs' work in order.

[2] *Dynamical Theory of Gases*, 3d edition, Chap. III, V, Cambridge, 1921.

and motion of every molecule of the gas. This is a tremendous simplification: the replacement of $2N$ points by a single point. The $6N$ dimensional space is called a "generalized" space and the point which determines by its position in this space the position and momentum of each molecule we shall call the "phase" point. Gibbs used the term "phase" to mean the state of the system as defined by the position and momentum of the individual molecules. The arrangement of the individual molecules in position is called the configuration of the system: and a state of the system in which the motion of each molecule is specified we shall call a "distribution" of momentum. A completely specified configuration and distribution then constitute a definite state or phase of the system. When we say that two otherwise identical systems differ in phase, we mean that they differ in some way in configuration or distribution or both. The extent of the difference depends upon how widely separated the two-phase points are in the generalized space. The reader should understand that we try to visualize this generalized space only by taking portions of two dimensions at a time. Thus in Fig. 10 a cross section shows the vertical momentum coördinates of two molecules and the phase point P indicates the actual momentum in a vertical direction for each molecule by its position.

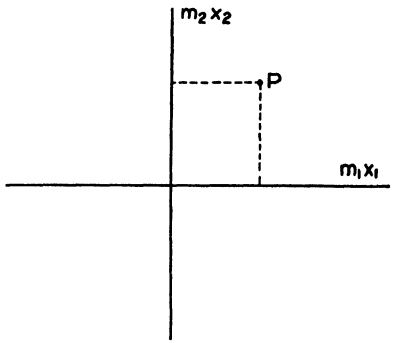


FIG. 10

Degrees of Freedom: As soon as we specify the position of a molecule along any coördinate axis, we admit the possibility of its motion in a direction parallel to this axis and are obliged to add a corresponding momentum coördinate to our system. Every independent positional coördinate thus implies a possibility of motion or a "degree of freedom." [1] Thus, our point molecule has three degrees of freedom. Suppose we assume that our molecule is a sphere of appreciable radius. Then, three coördinates will locate the center of the molecule in space but the orientation of the molecule will require the introduction of three additional angular coördinates and hence we would have six degrees of freedom. Furthermore, we can assign the coördinates in different ways but the total number is always the same. Thus, in a diatomic molecule the atoms of which are held rigidly with respect to each other, we may chose for the origin of angular coördinates either one of the atoms or the center of the line joining them or any other point in the molecule. The number of degrees of freedom of a system of molecules is equal to the sum of the number of degrees of freedom of each molecule, regardless of the manner in which we take the coördinates. Thus, we have already seen (p. 1151) that Debye in de-

[1] The reader will note that the terms "degree of freedom" and "phase" are being used in a manner quite different from their more familiar application in the study of the Phase Rule.

veloping his equation for heat capacity makes use of the fact that $3N$ coördinates completely determine the position of a body of N point molecules.

The Ensemble of Systems: We have seen that in a $6N$ dimensional generalized space a single "phase" point will define the exact position and motion of each part capable of separate motion, that is, of each degree of freedom. The system of particles which we are considering may be gaseous, solid or liquid and the particles may be molecules, atoms or electrons, charged or uncharged. If the system have kinetic energy, the phase point will be in motion. Concerning the actual path traveled by an individual point we can say nothing. The problem is too complex. We must resort to a more general method.

Let us suppose our generalized space to be filled with points, these points so close together that they form a dust and approach as a limit a continuous fluid medium to which we can assign the property of density. Each point represents an isolated system identical with all the others except for a difference in phase. This infinity of systems was called by Gibbs an "ensemble." Since the purpose of the conception of an ensemble is the study of the behavior of a single actual system, it is advantageous to imagine the ensemble as generated by a single system taking on, in turn, all the various energies, configurations and distributions of momentum possible to it. Each phase point of the ensemble then represents an isolated independent system and there can be no interaction between two such systems for they are really only two different phases of the same system. Two adjacent phase points represent two systems differing only slightly in phase.

Since the systems of the ensemble are isolated, the energy of each system must remain constant. A given phase point is constrained to travel in certain regions which we may designate as constant energy surfaces. Thus, the phase point of a monatomic gas system must move in the momentum portion of the generalized space on the surface of a $3N$ dimensional sphere of radius $\sqrt{2mE}$, where m is the mass of a single molecule and E the total energy of the gas. Furthermore, the laws of classical mechanics tell us that the quasi-fluid of points flows in certain fixed stream lines through the generalized space and Liouville's [1] theorem shows that the density of points along any stream line remains constant as the mass flows on. That is, there is no tendency for the points to crowd together or to disperse, and, if the distribution of points along any stream line is initially uniform, it will remain so. (It should be emphasized that these generalizations can only be made for positional and momentum coördinates. In place of momentum we might take velocity or kinetic energy as a coördinate but our important generalizations above would no longer apply.)

Finally, of course, there are many portions of the generalized space where the phase points cannot enter. Thus, if the molecules have volume, only one molecule can occupy a given place at one time. The phase points must be

[1] See Jeans, Dynamical Theory of Gases, 3d edition, p. 73, Cambridge, 1921. It is beyond the province of this chapter to discuss this theorem of mechanics.

excluded from regions which would imply interpenetration of molecules. These regions, however, need concern us no further, since they form a negligibly small part of the total generalized space.

The Canonical Distribution of Gibbs: From various considerations which we will discuss later, Gibbs was led to assume what he called a "canonical" distribution of the systems in an ensemble. The canonical distribution is one in which the density of the phase points in the generalized space is represented by the equation

$$D = Ke^{-E/kT}, \tag{62}$$

where E is the total energy of the system, k is the molecular gas constant and T is the absolute temperature.

The foregoing applies to the density of the phase points in the momentum portion of the generalized space. If the energy of a system depends also upon its configuration, i.e., if it has potential energy, we shall likewise assume a canonical distribution of the phase points in that portion of the generalized space that is defined by the positional coördinates. On the other hand, in the case of a monatomic gas, where the energy of the system is independent of its configuration, we shall assume a uniform distribution of phase points along the positional coördinates.

The Distribution Law for the Molecules of the Individual System: [1] We have assumed that the phase points which represent the systems of the ensemble are distributed in the generalized space according to equation (62). We shall next see what conclusion is to be drawn as to the manner in which the energy of an individual system is distributed among the molecules of which the system is composed. Since each system of the ensemble has an actual distribution different from any other, any conclusion we draw will of course only be a general statement as to the average condition of a system. Let us consider kinetic energy first. We have

$$E = \tfrac{1}{2}m_1\dot{x}_1^2 + \tfrac{1}{2}m_2\dot{x}_2^2 + \cdots + \tfrac{1}{2}m_n\dot{x}_n^2, \tag{63}$$

where $m_1, m_2, \cdots, m_n$ are the masses of the molecules associated with motions in the various degrees of freedom and $\dot{x}_1, \dot{x}_2, \cdots, \dot{x}_n$ are the components of the velocities along the coördinate axes $x_1, x_2, \cdots, x_n$.[2] We may then write (62) in the following manner:

$$D = Ke^{-\frac{1}{2}m_1\dot{x}_1^2/kT} \cdot e^{-\frac{1}{2}m_2\dot{x}_2^2/kT} \cdots e^{-\frac{1}{2}m_n\dot{x}_n^2/kT}. \tag{64}$$

Since the density of the phase points depends only upon their energies, they will be distributed symmetrically about the origin in the generalized space.

[1] The reader should be careful not to confuse the distribution of energy among a large number of systems with the distribution of the energy of a single system among the molecules of which it is composed.

[2] It is beyond the scope of this work to consider how the rotational energy of a molecule may be expressed as a sum of squares. Suffice to say it can be done.

The total number of systems represented by phase points in the momentum portion of generalized space will be obtained by successive partial integrations over all coördinates as in finding the mass of a solid of variable density,

$$N_S = K \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} e^{-\frac{1}{2}m_1\dot{x}_1^2/kT} d(m_1\dot{x}_1) \cdots e^{-\frac{1}{2}m_n\dot{x}_n^2/kT} d(m_n\dot{x}_n).$$

Let us perform all the integrations except for the coördinate $m_1\dot{x}_1$. Then we have

$$N_S = K' \int_{-\infty}^{+\infty} e^{-\frac{1}{2}m\dot{x}_1^2/kT} d(m_1\dot{x}_1). \tag{66}$$

This expression tells us that the number of points that project upon any portion of the momentum axis $m_1\dot{x}_1$ is proportional to

$$e^{-\frac{1}{2}m_1\dot{x}_1^2/kT}.$$

But the number of points that project on the portion of the axis $d(m_1\dot{x}_1)$ represents the number of systems in which the molecule m_1 has a momentum between $m_1\dot{x}_1$ and $m_1\dot{x}_1 + d(m_1\dot{x}_1)$. Hence the chance that the molecule m_1 have a momentum between $m_1\dot{x}_1$ and $m_1\dot{x}_1 + d(m_1\dot{x}_1)$ in a system chosen at random from a canonical ensemble is given by the expression

$$Ke^{-\frac{1}{2}m_1\dot{x}^2/kT} d(m_1\dot{x}_1).$$

The probability is the same for all the other molecules in the other degrees of freedom. Now, obviously, one molecule can only have one given value for its momentum in one direction at a given instant but if we have a large number of molecules each with the same probability of distribution, we should not expect all molecules to have the same momentum. We should expect on the average to find them distributed in momentum according to this probability.[1] In other words,

$$dN = Ke^{-\frac{1}{2}m\dot{x}^2/kT} d(m\dot{x}), \tag{67}$$

where dN is the number of molecules on the average which have a momentum between $m\dot{x}$ and $m\dot{x} + d(m\dot{x})$. Since $m\dot{x} = \sqrt{2m\epsilon}$, where ϵ is the kinetic energy of a molecule in a given degree of freedom, we may write equation (67) above

$$dN = Ke^{-\epsilon/kT} \frac{d\epsilon}{\sqrt{\epsilon}}. \tag{68}$$

This is our general distribution law which holds without restriction for a monatomic gas. If the potential energy is a function of the squares of the

[1] From (67) we see that a molecule has the greatest probability of having a momentum not greatly different from zero. The actual probability however is equal to the exponential term multiplied by $d(m_1\dot{x}_1)$, so that we should not expect to find many molecules with a value for momentum lying between any very narrow limits. This conclusion however takes no account of the quantum theory. See equation (42).

may be sure, however, that real physical systems behave in an extraordinarily uniform manner and that, from the molecular standpoint, variations in this behavior must be highly improbable since they are not impossible. Hence, when a system changes, it must ordinarily pass to a state of greater probability and the increase of entropy and the increase of probability must be related to each other. Boltzmann [1] was the first to elaborate this subject.

Probability: While the term probability may be used in different senses, technically it has one general underlying significance. The probability of an event depends upon the number of possible ways the event can happen. Thus, there is only one way that a hand of thirteen hearts can be made up at whist. There is an enormous number of ways in which a hand containing less than thirteen hearts may be made up. Hence, while the hand of thirteen hearts is just as likely to be dealt as any other specified hand, the probability of the all-hearts hand is so small as compared with the not-all-hearts hand that few players have ever seen the former. Probability is then to be defined in terms of the number of possibilities. It may be expressed in many different ways, but the underlying significance and the results are usually the same even though the mathematical forms may appear quite different. We shall find this especially true in considering the relation of entropy to probability.

Entropy as Function of Probability: Since entropy is a somewhat abstract quantity in itself and probability the only fundamental tendency that we can discern when we regard matter as made up of molecules, it becomes highly desirable to express entropy as a function of probability. The form of the function may be more or less optional and arbitrary but it will be convenient to choose a function that will be consistent with the ordinary usage of the term entropy. There are two main conditions to be complied with: (1) the entropy must increase as the probability increases; (2) the entropy must be additive, i.e., the entropy of two like systems taken together must be equal to the sum of the entropies of the separate systems. These conditions are satisfied very neatly if we define entropy by the following equation:

$$S = klnP + C, \tag{74}$$

where k is the molecular gas constant and P the probability. That the first condition is satisfied is obvious. That the second condition is satisfied becomes obvious if we write

$$S_1 + S_2 = klnP_1 + klnP_2 + C_1 + C_2 = klnP_1P_2 + C_1 + C_2.$$

For the probability of two separate states occurring together is equal to the product of their probabilities of occurring separately. Hence

$$S = klnP_{1,\,2} + C_1 + C_2, \tag{75}$$

where $P_{1,\,2}$ is the probability of the combined systems.

The classical illustration of entropy as a function of probability is the isothermal expansion of a gas. Let us suppose N molecules of a gas in a vessel

[1] Boltzmann, *Vorlesung über Gastheorie*, Barth, Leipzig, 1912.

divided by a partition into two equal compartments. The probability of any molecules being on one side of the partition is $\frac{1}{2}$. The probability of any two being in the same compartment is $(\frac{1}{2})^2$ and the probability of N molecules being together is $(\frac{1}{2})^N$. Hence the entropy of the gas when it is all on one side of the partition is given by

$$S = kln(\tfrac{1}{2})^N + C.$$

On the other hand, a molecule is certain to be on one side or the other of the partition and the probability that the gas is somewhere in the box is 1. Hence the change in entropy in expanding from the volume of $\frac{1}{2}$ the box to a volume equal to the box is

$$\Delta S = kln(1)^N - kln(\tfrac{1}{2})^N = kln2^N = Nkln2.$$

If $\mathbf{N}$ = Avogadro's number, $\mathbf{N}k = R$, $\Delta S = Rln2$. This is the value given by our thermodynamic equations.

Another simple demonstration of the connection between entropy and probability is to be found in the entropy of vaporization. Let us consider a molecule about to evaporate from the surface of a substance. Our distribution law (67) for kinetic energy tells that the probability of a molecule's existing with the kinetic energy ϵ_1 in a direction normal to the surface is given by the expression

$$Ke^{-\epsilon_1/kT}.$$

As the molecule leaves the surface it loses energy equal approximately to the internal energy of vaporization per molecule and its remaining energy we shall call ϵ_0. The probability for the molecule's existing with the kinetic energy ϵ_0 is now

$$Ke^{-\epsilon_0/kT}.$$

We have from equation (74)

$$\Delta S = klnP_2 - klnP_1 = \frac{k(\epsilon_1 - \epsilon_0)}{kT} = \frac{\bar{\epsilon}}{T}.$$

For N molecules

$$\Delta S = \frac{N\bar{\epsilon}}{T} = \frac{E}{T},$$

where E is the internal energy of vaporization per mol. Our knowledge of the mechanism of evaporation is too imperfect to elaborate upon the rather crude illustration.

We have been discussing changes of entropy in relation to changes in probability. We have already learned that entropy is one important quantity to which an absolute value may be assigned. We are not compelled to speak of the value of entropy with respect to an arbitrary zero as in the case of energy. While we have written (74) with an arbitrary constant C, we may expect that, if the complete probability of the system is expressed, C will become zero.

The question is, therefore, how can the total probability P be expressed? So long as we are dealing with changes in entropy, this is not important, provided the two probabilities are expressed in the same way, since it is the ratio of the probabilities with which we are concerned. But, if we are going to use equation (74) without the constant to express absolute entropy, then we must seek some form of probability expression which will be absolute, if such is to be found.

The convential form of expressing probability is as a proper fraction. Thus the chance of throwing a six and four with two dice is 2/36: there being 36 different ways the two dice can fall and two of these ways giving a six and a four. But we might say that the chance of throwing a six and a four was simply 2, there being two ways that it can be done. The reason for using the fraction is that we were interested in the relative probability: if we omit the denominator, we shall have the absolute probability, the number of ways or possibilities for the chosen event to happen. We shall find that this is the kind of probability that we are concerned with in the absolute value of entropy. Planck [1] introduced this conception of probability. From this point of view, the probability of a certain specified state of system is not a proper fraction but is equal to a large whole number, viz., the total number of arrangements possible to produce the specified "state" of the system. In other words, Planck omitted the denominator which was equal to the total sum of possibilities.

Entropy and Probability for a System of Harmonic Oscillators: We have two illustrations of the correlation of entropy and probability in which the probabilities were of different sorts and we have referred to the number of "arrangements" possible to a system in a specified state without indicating what is to be "arranged." Lest the reader conclude that probability is always to be applied in a haphazard or vague manner, let us hasten to say that we shall show later how the probability of any system may be defined in a perfectly general way. For the present we wish to illustrate the application of the Planck idea of absolute probability to a system. An excellent example is the case of the so-called "ideal" monatomic solid or system of ideal linear oscillators. For such a system it follows from the Einstein equation (46) that the total number of quanta of energy at any temperature is

$$n = \frac{N}{e^{\epsilon/kT} - 1}, \tag{76}$$

where ϵ is the value of a single quantum. The "specified state" of our system is that the temperature have some certain value. This implies that the energy of the system is constant and equal to the number of quanta given by the expression above. The different arrangements possible to this system consist of the different ways n quanta of energy may be distributed among N atoms. This is the same problem as if we were trying to find all the different ways

[1] Wärmestrahlung, 4th edition, p. 111, Barth, Leipzig, 1921.

that we could place n balls in N boxes, allowing the possibility of putting any number of balls up to the total number in any given box but not distinguishing between different balls. The problem is a simple one in theory of probability [1] and the number of possible arrangements is

$$P = \frac{(n + N - 1)!}{n!\,(N - 1)!}. \tag{77}$$

The absolute entropy of the system then should be given by the equation

$$S = klnP = kln\frac{(n + N - 1)!}{n!\,(N - 1)!}. \tag{78}$$

For large numbers

$$n! = n^n e^{-n},$$

and substituting in equation (76), the above expression reduces to

$$S = Nk\left[\frac{\frac{\epsilon}{kT}}{e^{\epsilon/kT} - 1} - ln(1 - e^{-\epsilon/kT})\right],$$

precisely the result obtained (55) by the integration of $\int_0^T C_v dlnT$ for such a system. This is a remarkable illustration of the fact that entropy is only a function derived from the probability of a system.

One point in this connection calls for comment. We have calculated all the possible arrangements for the system at constant energy. We have seen, however, that distributions of energy differing appreciably from the distribution law (42) (as for instance one oscillator having all the energy) rarely or never happen. Should not some account be taken of this? The answer is readily given. Any one arrangement appears to be as likely to happen as any other and the distribution law is true because all but a negligible fraction of the enormous number of arrangements possible correspond to this normal distribution. The numerical result will not be appreciably different whether we take all the possible arrangements or only those corresponding to the distribution law, but the absolute probability should include all the possible distributions of the energy.

As was pointed out before, equation (55) gives the entropy for a monatomic solid except for a correction term for the "compound" quanta. If we knew the number and magnitudes of these, we could easily set up the expression for the exact entropy from the absolute probability.

If the kinetic energy of a solid is zero at the absolute zero of temperature, then there is only one possible distribution.[2] The absolute probability is one

[1] Whitworth, Choice and Chance, 5th edition, p. 90, Beland Co., Cambridge, 1901.

[2] In the absence of all kinetic energy, it may be felt by some that the absolute probability can no longer be defined.

and the absolute entropy is zero. The third law appears as an obvious generalization. The case of supercooled liquids and solutions offers difficulties which we shall consider later.

The Entropy of Monatomic Gases

The most important application of the idea of absolute probability is to be found in the calculation of the entropy of monatomic gases. Here we have an experimentally verified relation of importance second only to the third law itself. The Nernst school of thermodynamicists are accustomed to speak in terms of the "chemical constant" of monatomic gases but as will be shown the "true" chemical constant bears a simple relation to the entropy constant. We have for the "true chemical constant," equation (10),

$$lnp = -\frac{\Delta H_0}{RT} + \int \frac{\int_0^T \Delta C_p dT}{RT^2} dT + i.$$

For a monatomic gas, $C_p = \frac{5}{2}R$. If we substitute this value in (10), we get

$$lnp = -\frac{\Delta H_0}{RT} + \tfrac{5}{2} lnT - \int \frac{\int_0^T C_{p_s} dT}{RT^2} dT + i. \tag{79}$$

Integrating by parts,

$$\int \frac{\int_0^T C_{p_s} dT}{RT^2} dT = -\frac{\int_0^T C_{p_s} dT}{RT} + \int_0^T \frac{C_{p_s}}{RT} dT;$$

also from (9)

$$\Delta H = \Delta H_0 + \tfrac{5}{2}RT - \int_0^T C_{p_s} dT.$$

Substituting in (79),

$$lnp = -\frac{\Delta H}{RT} + \tfrac{5}{2} lnT - \int_0^T \frac{C_{p_s} dT}{RT} + \tfrac{5}{2} + i. \tag{80}$$

If we multiply through by $-R$ and rearrange, we get

$$\tfrac{5}{2}RlnT - Rlnp + (\tfrac{5}{2} + i)R = \frac{\Delta H}{T} + \int_0^T \frac{C_{p_s}}{T} dT. \tag{81}$$

But the right hand side of the equation represents the entropy of the saturated vapor of a crystalline solid at the temperature T. Hence we may write

$$S = \tfrac{5}{2}RlnT - Rlnp + S_0 = \frac{\Delta H}{T} + \int_0^T \frac{C_{p_s}}{T} dT.$$

In short,

$$S = \tfrac{5}{2}RlnT - Rlnp + S_0, \tag{82}$$

where S is the entropy of a monatomic gas and

$$S_0 = (\tfrac{5}{2} + i)R. \qquad (83)$$

Equation (83) shows the relation between the true chemical constant and the entropy constant of a monatomic gas.[1] Since most of the theoretical speculations have been based on probability considerations, it is more direct and logical to discuss the question in terms of the entropy constant. A number of investigators [2] have derived expressions for this constant by various methods of reasoning. The first expression which gave satisfactory agreement with experimental data was obtained by Tetrode. Tetrode took the original formula of Gibbs for the entropy of a monatomic gas and by a simple application of the quantum theory (actually nothing but the insertion of Planck's h) he obtained surprising agreement with the experimental values. We shall follow our own mode of reasoning in developing this formula.

Gibbs [3] pointed out that the entropy of any system, gas, solid, etc., could be identified with the logarithm of what he called the extension in phase. By extension in phase is meant the entire volume of the generalized space which is occupied by the phase points of an ensemble of systems. If we limit our consideration to monatomic gases, then the energy depends simply on the momentum coördinates. That part of the extension in phase which is due to the space coördinates becomes simply V^N, where V is the volume of the vessel in which the gas is actually contained and N is the number of molecules. Obviously the shape of the vessel can have no significance. The evaluation of the extension in momentum is not quite so simple.

Instead of proceeding to calculate the volume of the extension in phase as did Gibbs, we shall do something slightly different. We shall calculate the total number of phase points in an ensemble at a given temperature. The significance of this in terms of probability is at once obvious. Each phase point of an ensemble corresponds to a definite possible condition or state of the given system. The total number of phase points then represents the total number of possible arrangements of the given system for a given temperature and volume, or in other words the probability of the system. We have already, in equation (70), set up the integral for the number of systems on the ensemble. The expression contains, however, an arbitrary constant which depends upon the absolute density of the phase points, this density of course varying with the energy according to the exponential law of the canonical distribution. In so far as the relative probability is concerned, we will get consistent results so long as we use a constant value for K_0, but we cannot expect to get an

[1] It is the constant in equation (79) to which Nernst applied the term "chemical constant." The 5/2 in equation (83) is the coefficient of RT in the equation connecting ΔH and ΔH_0. Conceivably for polyatomic gases this coefficient might differ from 5/2.

[2] Sackur, *Ann. Physik.*, (4) **40**, 67 (1913). Tetrode, *Ann. Physik.*, (4) **38**, 434 (1912); **39**, 255 (1913). Lewis, *Phys. Rev.*, (2) **18**, 121 (1921).

[3] Elementary Principles of Statistical Mechanics, p. 170, Yale University, New Haven, 1914.

absolute value of probability with an undetermined constant in our equation. Furthermore, we cannot even be satisfied with the relative probability of two systems, for, so far as we have seen at present, a monatomic gas may take on an infinite number of conditions or states each differing from the other by as small an amount as we please. This means that a given ensemble would contain an infinite number of phase points, the infinity being of the same kind as the number of points in a line. The mathematician is not satisfied to say that if line CD is twice as long as line AB, CD contains twice as many points as AB, for a line cannot be made up of points at all. So one may reason that if the change of entropy from state I to state II is to be a definite measurable quantity, then the probability of state II should bear a finite ratio to state I. In other words, the density of the phase points of an ensemble in the generalized space should not be infinite at any point. Liouville's theorem derived from the classical mechanics tells us that the density of phase points remains constant along a constant energy surface and this constant may very well be a fundamental constant of nature. It is at this point that the quantum theory comes to our rescue with its fundamental assumption that a system changes its state by definite finite amounts.

In our application of the quantum theory to the monatomic solid we had the rule laid down by Sommerfeld[1] that the area of momentum times the length passed over by a phase point in one complete cycle must be an integral multiple of h. Or, mathematically stated (37),

$$\oint mV dS = nh.$$

The molecules of a gas, however, do not perform cyclical motions. How can we apply a principle which assumes that a molecule returns to its original position after a certain interval of time or period?

We can state what appears to be the underlying principle of equation (81) in another way. Liouville's theorem in its most elementary form states that if we divide our generalized space into cells of equal volume and place one phase point in each cell, then after a period of time there would still be one phase point in each cell, although not of course the same phase point that was there originally. But these cells are of the dimensions $(mVS)^{3N}$, which are the dimensions of h^{3N}. We may then assume that space is divided into cells, each cell being bounded by surfaces of area $= h$, and that each cell corresponds to one phase only of the system. Reduced to two dimensions, this assumption is similar to (37). Whether a phase point passes continuously from one cell to another or not, i.e., whether a system changes its phase continuously or discontinuously, is a question we are not prepared to answer.[2] It may be that our generalized space is a network and the phase points may only travel along the lines of this network.

Be this as it may, our quantum assumption tells us that the density of systems in the ensemble cannot be infinite, but that the maximum number of

[1] Sommerfeld, Atombau und Spektrallinien, 3d edition, p. 243, Friedr. Vieweg and Son, Braunschweig, 1922.

[2] See Planck, Wärmestrahlung, 4th edition, p. 188, Barth, Leipzig, 1921.

phase points is reached when one occurs per each unit of (momentum times length)^{3N}, the units being equal in volume to the Planck constant h^{3N}. This indicates that the density of points is equal to $\frac{1}{h^{3N}}$, and is not a variable quantity as assumed in the canonical distribution of Gibbs. It will be remembered, however, that all but a negligible portion of the systems of the canonical ensemble have the same energy and hence are distributed with a uniform density; so that we may, for mathematical convenience, use the canonical distribution, knowing that the results will be identical with those for an ensemble of systems of constant energy. It is only necessary that our formula correspond to the proper density for systems of the average energy. By equation (62),

$$D = Ke^{-E/kT}.$$

For an ensemble corresponding to a monatomic gas containing N molecules, and at a temperature T the average energy $\overline{E}$ is by the equipartition law

$$\overline{E} = \tfrac{3}{2}NkT.$$

For one mol. of gas

$$N = 6.061 \times 10^{23}.$$

The density of the systems having the average energy is by our quantum assumption

$$D = Ke^{-3NkT/2kT} = \frac{1}{h^{3N}}.$$

Hence

$$K = \frac{e^{3N/2}}{h^{3N}},$$

$$D = \frac{e^{3N/2}}{h^{3N}} e^{-E/kT}.$$

We are now ready to integrate the density over the whole generalized space in order to obtain the total number of phase points in the ensemble. For the space coördinates we have simply to multiply by V^N. For the momentum coördinates we have equation (70). Since we wish to calculate the absolute probability, we must insert the values for all constants. This leads to the rather formidable expression

$$P = \frac{V^N e^{3N/2}}{h^{3N}} \int_0^\infty e^{-E/kT} \frac{(2mE)^{(3N-1)/2}(\pi)^{3N/2}}{\frac{1}{2}\left(\frac{3N}{2}\right)^{(3N/2)-1} e^{-3N/2}} d\sqrt{2mE}.$$

If we make the substitution

$$\frac{E}{kT} = X^2,$$

and the kinetic energy $\frac{1}{2}mr^2\omega^2$ would be of the order of magnitude of 10^{-11} ergs. But the average translational energy of a molecule is only 10^{-13} ergs, so that, if a monatomic molecule were to have even one quantum of energy, it would have many times the average energy per molecule. It follows from our distribution law (68) that the number of monatomic molecules having rotational energy will be small and their total energy negligible.

For the diatomic molecule the case is otherwise. The diatomic molecule is commonly assumed to resemble a miniature dumbbell in shape. The two atoms may be supposed to occupy equilibrium positions at an appreciable distance from each other. They are prevented from separating by strong attractive forces, and, if they approach more closely to each other, repulsive forces come into play. This gives a more or less rigid structure. The same quantum considerations apply to rotation around the line joining the centers of the two atoms as an axis as hold in the case of the monatomic molecule. We should not expect many of the molecules to have energy of rotation around this axis. Around the two axes, at right angles to the line of centers, the moment of inertia of the molecule will be large; hence, by equation (89), the quantum of energy is small and we should expect a diatomic gas to have a considerable amount of energy of rotation. This is confirmed by the facts. The diatomic gases at higher temperatures show a heat capacity at constant volume in the neighborhood of $\frac{5}{2}R$, indicating at least two rotational degrees of freedom. At lower temperatures this heat capacity falls off and in the case of hydrogen near its boiling point the heat capacity corresponds to that of a monatomic gas. Liquefaction intervenes so that we cannot observe this extreme phenomenon in the case of the other diatomic gases. The variation of the heat capacity of all diatomic gases, however, indicates that some sort of quantum theory must be introduced to explain the acquisition of rotational energy. It has been pointed out by Kemble and Van Vleck[1] that, even according to the classical mechanics, the rotational specific heat would not be exactly constant. The equipartition law requires the energy RT for the two rotational degrees of freedom but, in addition, if the molecule be not absolutely rigid, we may expect a slight stretching due to the centrifugal force, which would mean the acquirement of potential energy. This potential energy would be roughly proportional to the square of the kinetic energy.

If the forces holding the atoms together are elastic, there is the possibility of an oscillation in the line of centers. The molecule could be treated as the equivalent of a simple harmonic oscillator and the energy by the quantum theory must be an integral multiple of $h\nu$. For molecules composed of light atoms, such as hydrogen, the forces holding the atoms together are believed to be very great and the frequency of oscillation is very high. This would make the quantum of energy very large and we should expect to find very little energy of oscillation in these molecules at ordinary temperatures. For heavy atoms held together by weak constraints as in the case of iodine molecules it is likely that a considerable amount of energy is to be found in the form of

[1] *Phys. Rev.*, 21, 653 (1923).

oscillations. This energy would be, on the average, half potential and half kinetic, and, according to the principle of equipartition, should be equal to RT. We should thus expect that, at some higher temperature, the diatomic gases would appear at least to approach a value for C_v of $\frac{7}{2}R$. In addition to the above motions, Kruger [1] has suggested the possibility of gyroscopic motions for the dumbbell model of the diatomic molecule. His ideas on the subject are interesting but his predictions do not appear to be confirmed by experiment.

The Quantization of the Rotational Degrees of Freedom: The application of the quantum theory to any atomic process always appears artificial and arbitrary. If the correct results are not obtained in one way, a different assumption is made and the application is more or less of a cut and try process. It is so much so at times that the reader may well wonder whether the whole quantum theory with its remarkable achievements may not be a magnificent piece of self deception produced by the scientific imagination. When we come to consider the quantization of the rotational orbits, we find the application of the quantum theory especially uncertain and unsatisfactory.

In the first place, while the diatomic molecule has two rotational degrees of freedom, its statistical condition so far as quantum conditions are concerned is determined by a single quantity, viz., its kinetic energy. That is to say, while two angles must be specified before the position of the molecule is fixed, so long as the molecule is undisturbed, it spins with a constant energy in a fixed plane. The position of this plane cannot be of significance in the quantum relations, and we have only the energy to consider and to guide us in the application of the quantum conditions. Planck has designated a case like this, where, so far as the quantum theory is concerned, two degrees of freedom merge into one, by saying that the two degrees of freedom are "coherent."

The most successful approach to a solution of this problem has been made by Reiche.[2] Reiche considered the effect of a gravitational field on the spinning molecule, under which condition the molecule no longer spins in a fixed plane but its motion is broken up in such a manner that the quantum conditions may be applied by a consideration of two degrees of freedom. He actually considers the motion of a spinning top, inferring that, as the gravitational field is weakened, the top will approach the condition of the spinning molecule as a limiting state. As a result of these considerations, he obtains for the energy of rotation the following expression:

$$\epsilon = \frac{h^2(n_1 + n_2)^2}{8\pi I^2}, \tag{90}$$

where h is Planck's constant, n_1 and n_2 are the quantum numbers for the two degrees of freedom and I is the moment of inertia of the molecule. The number of molecules in a given quantum condition is then given by an equation of the following form:

$$N_{n_1 n_2} = p_{n_1 n_2} e^{-\epsilon_{n_1 n_2}/kT}. \tag{91}$$

[1] *Ann. Physik.*, (4) **51**, 450 (1916).

[2] Reiche, *Ann. Physik.*, (4) **58**, 657 (1919).

This will be recognized as the distribution law (42) as given by the quantum theory and further modified by the "coefficient of probability" $p_{n_1 n_2}$, which may have different values for different quantum states. The total rotational energy of the molecules will be given by a similar expression to the one we found (45) in deriving the Einstein equation

$$E = N \frac{\sum_{n_1} \sum_{n_2} p_{n_1 n_2} \epsilon_{n_1 n_2} e^{-\epsilon_{n_1 n_2}/kT}}{\sum_{n_1} \sum_{n_2} p_{n_1 n_2} e^{-\epsilon_{n_1 n_2}/kT}},$$

where the summation signs mean that all possible values in combination of n_1 and n_2 are to be included. The rotational heat capacity at constant volume C_r is obtained by differentiating the above expression with respect to the temperature. The resulting expression becomes simple at very high and very low temperatures. At intermediate temperatures Reiche evaluates it as a series.

When equal probability is assumed for all quantum states, the equation obtained for C_r behaves in a very peculiar manner, rising to a maximum at a certain temperature and then falling again, Curve (I), Fig. 12. This does not

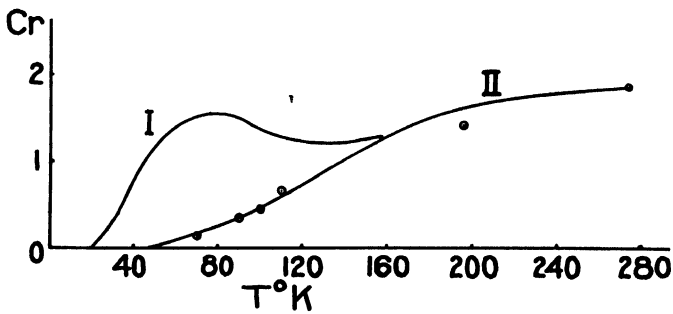


FIG. 12

correspond to the rotational heat capacity of a diatomic gas, which increases continually with the temperature. In order to obtain an equation which gives a fair approximation to experiment for hydrogen, Reiche was compelled to assume the nonexistence of certain states of quantum number zero, which means that no molecule can rotate in a vertical plane in a gravitational field. It also implies that all molecules have at least one quantum of rotational energy at all temperatures. When this assumption is made, he can, by a proper choice of constants, reproduce the heat capacity curve for hydrogen with considerable fidelity [Curve (II), Fig. 12]. Kemble and Van Vleck[1] have recently developed a formula for the heat capacity of hydrogen following the general lines that Reiche pursued, but taking account of an additional degree of freedom due to the vibrational energy of the atoms along the line of centers.

[1] *Phys. Rev.*, 21, 653 (1923).

In order to quantize this oscillation, it is necessary to assume a law of force between the atoms. The law of force that they assume is of the form

$$f = \frac{a(r - r_0)}{r^3} . \tag{92}$$

Here a is a constant, r the distance between the nuclei of the atoms and r_0 the equilibrium distance. From this assumption, they derive an expression for the specific heat of hydrogen which contains an extra adjustable constant and, in addition, gives a higher value for C_v at the higher temperatures, due to the oscillatory degree of freedom. With this equation they are able to fit the experimental data over the entire experimental range from 0 to 1300° K. An equation which involves so many assumptions, however, can scarcely be regarded as other than a fortunately chosen empirical expression.

The Calculation of Entropy for the Diatomic Gases: Tetrode,[1] Sackur[2] and others have derived a theoretical relation for the entropy of a diatomic gas by the same methods of reasoning that are used in the cases of a monatomic gas. They obtain the equation

$$S = RlnT^{5/2}M^{3/2}VI + S_0,$$

where I is the moment of inertia of the molecule and M the molecular weight. This involves the assumption that the gas has two rotational degrees of freedom in addition to the three translational degrees of freedom. It will be observed that I is a constant characteristic for the molecule in question and like the fundamental frequency ν_0 of a monatomic solid is not to be calculated from any simple fundamental properties such as atomic weight. Tolman[3] has also shown that the entropy of a diatomic gas is given with considerable accuracy by the equation (85) for the entropy of a monatomic gas plus the integral

$$\int_0^T C_r dlnT,$$

where C_r is the excess heat capacity of a diatomic gas over that for the monatomic gas. The integral

$$\int_0^T C_r dlnT$$

can only be evaluated in the case of hydrogen, since the heat capacities of the other gases as we have mentioned before do not fall to the monatomic value above their liquefaction temperatures.

In the case of the alkali halides, we saw that the frequency could be calculated from the optical properties of the crystal. In a recent paper Urey[4]

[1] *Ann. Physik.*, (4) **38**, 441 (1912).
[2] *Ann. Physik.*, (4) **40**, 87 (1913).
[3] *J. Am. Chem. Soc.*, **42**, 1185 (1920).
[4] *J. Am. Chem. Soc.*, **45**, 1445 (1923).

has shown that the moment of inertia I for the diatomic molecule may be calculated in many cases successfully from the constants for the band spectra. In calculating the moment of inertia he uses the classical formula

$$I = kT\left[\frac{\lambda_1\lambda_2}{\pi c(\lambda_2 - \lambda_1)}\right]^2, \tag{93}$$

where $\lambda_1\lambda_2$ are the maxima of the band and c is the velocity of light. It might be anticipated that the quantum theory of band spectra should furnish a more exact value for I.

In order to check the value of the moment of inertia obtained in this manner, Urey calculated the entropy for a number of diatomic gases by the method of Tolman described above. In order to evaluate the integral

$$\int_0^T C_r d\ln T,$$

he uses Reiche's formula for C_r, substituting his value of I in the expression for the energy (90). The value of the entropy obtained in this way is compared with the value calculated in the ordinary way from thermal data. For hydrogen, nitrogen, hydrogen chloride and carbon monoxide he gets a striking agreement with the experimental data. For other gases such as oxygen he is less successful. It is very likely that a more general equation of the type proposed by Kemble and Van Vleck would give better agreement for some of these gases.

It will be seen we have scarcely progressed beyond stating the problems to be solved before the heat capacities of diatomic gases can be satisfactorily explained. For polyatomic gases with their additional degrees of freedom in the molecule the problems become still more complex.

Some Applications of the Third Law and the Chemical Constant

Dissociation of Hydrogen: Nernst, in his book on the heat theorem, pointed out that the chemical constant could be used to calculate the heat of dissociation of hydrogen. Isnardi [1] and later Edgar [2] have discussed the dissociation of hydrogen at some length. We will indicate briefly the manner in which the calculation is made. Let us consider the reaction

$$H_2 \rightarrow 2H.$$

We have the fundamental thermodynamic equation

$$\Delta F - \Delta H = -T\Delta S.$$

Langmuir [3] has measured the dissociation of hydrogen at high temperatures. It is not likely that ΔF, as calculated from any of his individual measurements, is

[1] *Z. Elektrochem.*, **21**, 405 (1915).
[2] *J. Am. Chem. Soc.*, **45**, 673 (1923).
See also Lewis and Randall, Thermodynamics, p. 458, McGraw-Hill Co., New York, 1923.
[3] *J. Am. Chem. Soc.*, **37**, 417 (1915).

in serious error. ΔH, as calculated from the temperature coefficient of the dissociation [equation (13)], may however be very uncertain. On the other hand, by calculating ΔS we may obtain a far greater accuracy for ΔH from the thermodynamic equation. The entropy of the monatomic hydrogen is of course readily obtained from the Gibbs-Tetrode formula. The entropy for diatomic hydrogen may be obtained from the thermal data alone, but, because of the uncertainties of the heats of fusion and vaporization of hydrogen at the very low temperatures at which they must be measured, more accurate results can be obtained by the method (p. 1190) proposed by Tolman. On the other hand, we may calculate ΔH from data obtained from ionization potential measurements. If this result is correct, as is now believed, we may then calculate the degree of dissociation with a higher accuracy than can be obtained by direct measurement.

Thermal Ionization: Nernst also pointed out the possibility of calculating the thermal ionization of gases from chemical constants. Saha [1] and Tolman [2] have discussed the reaction

$$M \rightarrow M^+ + \text{electron}$$

at some length. If we consider a metal at the temperature of the sun where atom, ion and electron may all be considered in the gaseous state at pressures sufficiently low to be treated as perfect gases, then the Gibbs-Tetrode formula gives the entropies for these different constituents. The ionizing potential gives a measure of ΔH and since ΔH may without great error be supposed to be independent of the temperature, we can readily calculate the percentage ionization by thermodynamics for metals like cæsium whose ionizing potentials are known.

The Entropy of Electron Gas: When a metal is heated to a sufficiently high temperature, electrons are emitted in a manner that appears exactly analogous, from the standpoint of the kinetic theory, to the evaporation of molecules from the surface of a solid. There appears to be a definite heat of evaporation and a definite vapor pressure of electrons which increases with the temperature according to the well-known thermodynamic laws. Laue [3] has shown that, under suitable conditions, the swarm of electrons emitted may be treated as a gas. Since the electrons repel each other, this gas will deviate from the gas laws in the opposite direction from most gases. If the electron gas be sufficiently dilute, which is of course true under all experimental conditions, it may be treated as a perfect gas without appreciable error. Since the vapor pressures obtained experimentally are so small, it is not possible to measure them directly. They are readily calculated however from the "saturation current." By the saturation current is meant the limiting current emitted by a hot filament as the applied negative potential between it and a grid is indefinitely increased. This gives the rate of evaporation of electrons. Now, for a filament in equilibrium with electron gas, the rate of evaporation must be

[1] *Phil. Mag.*, **40**, 472 (1920).
[2] *J. Am. Chem. Soc.*, **43**, 1630 (1921).
[3] *Ann. Physik.*, (4) **58**, 695 (1919).

equal to the rate of condensation. If no electrons are reflected from the filament, the rate of condensation is equal to the number of electrons colliding with the filament. From the kinetic theory of gases,[1] n, the number of electrons colliding with the filament per cm.^{2} per second, is given by the equation

$$n = \frac{p}{\sqrt{2\pi mkT}}, \tag{94}$$

where p is the vapor pressure of the electron, m is the mass of the electron and the other symbols have the usual significance. The number evaporating is given by

$$n = \frac{I}{\epsilon}, \tag{95}$$

where ϵ equals the charge of the electron in electromagnetic units and I is the saturation current. Combining these two expressions,

$$p = \frac{I\sqrt{2\pi mkT}}{\epsilon}. \tag{96}$$

The application of the third law and the equation for the entropy of monatomic gases to electron gas has been made by Nernst,[2] Tolman [3] and others. Recently Dushman [4] has applied these principles in a way that is especially adapted to experimental verification, by deriving a formula for the saturation current as a function of the temperature. We have equation (79) for the true chemical constant of a monatomic gas,

$$lnp = -\frac{\Delta H_0}{RT} + \tfrac{5}{2} lnT + \int_0^T \frac{C_{p_s} dT}{RT} + i,$$

where the value of i by the Gibbs-Tetrode equation is given by the relation

$$i = 10.17 + \tfrac{3}{2} lnM,$$

when M is the atomic weight of the electron. Dushman assumes that the heat capacity of the electrons in the metal is negligible so that the fourth term of the equation above disappears. We then have

$$p = M^{3/2}T^{5/2}e^{-(\Delta H_0/RT)+10.17}; \tag{97}$$

combining with (96),

$$I = \frac{\epsilon m N^{3/2}T^2}{\sqrt{2\pi k}} e^{-(\Delta H_0/RT)+10.17} = 60.2T^2e^{-\Delta H_0/RT}. \tag{98}$$

[1] Jeans, Dynamical Theory of Gases, 3d edition, p. 121, Cambridge, 1920.

[2] Die theoretischen und experimentallen Grundlagen des neuen Wärmesatzes, p. 154, Halle, 1918.

[3] *J. Am. Chem. Soc.*, **43**, 1592 (1921).

[4] *Phys. Rev.*, **21**, 623 (1923).

Dushman claims for this equation a very good agreement with experimental data and expresses confidence that it will be found to hold for all metals when more accurate data are available. The most accurate data at present available are for tungsten and here the agreement is certainly satisfactory. He is in doubt as to the exactness of the chemical constant i as calculated from the Gibbs-Tetrode equation, but he is quite sure that when this constant is known exactly, the equation (98) will give the rate of electron emission as a function of the temperature for all metals. The agreement obtained is a remarkable confirmation of the relations from which the equation was derived. As we have already noted, Dushman assumes the heat capacity of the electrons in the metal to be negligible. It is not likely that this assumption will cause serious error in the result obtained but it should be noted that the assumption can not be strictly true, else we should have no thermoelectric force. This can be demonstrated in the following way. By the well-known equation of thermodynamics, the work of removing a gram of electrons from one metal to another is

$$\Delta F = RT\ln\frac{p_2}{p_1}, \tag{99}$$

where p_1, p_2 are the vapor pressures of the electrons from the two metals. The contact difference of potential ϵ is related to this work by the equation

$$-23{,}074\epsilon = \Delta F. \tag{100}$$

Now the thermoelectric force is the temperature coefficient of contact potential.[1] Hence differentiating (100) and substituting the value of p_1 and p_2 from Dushman's equation, we have

$$-23074\frac{d\epsilon}{dT} = \frac{d(\Delta H_1 - \Delta H_2)}{dT} = 0. \tag{101}$$

This result is of course quite at variance with the facts. It is evident that ΔH, the heat of vaporization of the electrons, must be a different function of the temperature for different metals.

In discussing the heat capacities of metals, we noted the anomalous behavior of the electropositive metals and mentioned the theory that the deviation from the regular curve is due to the heat capacity of the free electron in the metal. Latimer [2] has recently attempted to prove this excess heat capacity to be due to the electron, by an ingenious process of reasoning in which he identifies the excess heat capacity of the metals with the temperature coefficient of the thermoelectric force. If we consider a reaction as above which involves the transfer of a gram mol. of electrons from a first metal to a second, we have

[1] Strictly speaking, a thermocouple is not a reversible system since heat flows from the hot to the cold junction. Presumably, however, the assumption of reversibility does not lead us far astray.

[2] *J. Am. Chem. Soc.*, **44**, 2136 (1922).

by thermodynamics

$$-23{,}074\frac{d\epsilon}{dT}=\frac{d\Delta F}{dT}=\frac{\Delta F-\Delta H}{T}\cdot \tag{102}$$

Differentiating a second time with respect to temperature, we obtain

$$-23{,}074\frac{d^2\epsilon}{dT^2}=\frac{1}{T}\frac{d\Delta F}{dT}-\frac{1}{T}\frac{d\Delta H}{dT}-\frac{\Delta F-\Delta H}{T^2}\cdot$$

From (102) this reduces to

$$23{,}074\frac{d^2\epsilon}{dT^2}=\frac{1}{T}\frac{d\Delta H}{dT}\cdot \tag{103}$$

But

$$\frac{d\Delta H}{dT}=\sigma_2-\sigma_1, \tag{104}$$

where σ_1 and σ_2 are the heat capacities of the free electrons in the two metals. Hence

$$23{,}074\frac{d^2\epsilon}{dT^2}=\frac{\sigma_2-\sigma_1}{T}\cdot \tag{105}$$

Latimer identifies σ with the positive deviation of the heat capacity of a metal from the regular curve, Fig. 8, and, by measuring the thermoelectric force of the various metals against silver, which appears to be a perfectly "regular" metal, he finds an excellent qualitative agreement between the data for the two quantities in (105). The data are hardly of sufficient accuracy to show a very exact agreement even if one is to be expected. In making the actual comparisons, he finds it advantageous to integrate equation (105) with respect to the temperatures, obtaining

$$23{,}074\left[\left(\frac{d\epsilon}{dT}\right)_2-\left(\frac{d\epsilon}{dT}\right)_1\right]=\int_0^T\frac{(\sigma_2-\sigma_1)}{T}dT. \tag{106}$$

The right side of this equation is the difference of the areas between the actual and theoretical curves for a pair of metals. He calls these areas the entropy of the electrons in the metal. In making the comparisons, he finds it necessary to assume only one equivalent of electrons per gram atom even for magnesium and aluminium. This appears at first thought a rather surprising result and it may be that his conclusion is unwarranted from the available data.

On the other hand, there is an alternative view of the matter which makes this conclusion less surprising. It is, of course, perfectly obvious that the abnormalities of the heat capacities are due to the presence of the electron. Remove the electron and the metallic ion has a heat capacity which will be found without doubt to be normal. This is, however, not proof that the electron is acquiring, independently of the atom, an appreciable kinetic energy in the metal.

We have from equation (102), for a reaction involving the transfer of an equivalent of electrons from one metal to another,

$$-23{,}074\frac{d\epsilon}{dT} = \frac{d\Delta F}{dT} = -\Delta S.$$

It may very well be that so far as ΔS is concerned this reaction is equivalent to the following reaction:

$$M_1 + M_2^+ \rightarrow M_1^+ + M_2,$$

where M is a metal and M^+ a metallic ion. Now, by the third law, for this reaction

$$\Delta S = \int_0^T \frac{\Delta C_p dT}{T}$$

and the latter integral is the one that Latimer measured by the integral

$$\int_0^T \frac{(\sigma_2 - \sigma_1)}{T} dT.$$

Since any metallic atom would probably become normal in its heat capacity on the loss of one electron, we would need to consider only one equivalent of electrons per gram atom even for magnesium or aluminium. The agreement of thermoelectric data with deviations in the heat capacity curves would then be a thermodynamic consequence and we can scarcely hope to prove anything about the mechanics of matter by thermodynamics.

The Problem of Gas Degeneration

Since we have found it necessary to quantize the motions of atoms in every physical state of combination with each other in order to explain their behavior, it may be anticipated that sooner or later we shall try to quantize the motions of the monatomic gas molecules. Indeed, we have already done so. The lack of a rotational degree of freedom is explained by the quantum theory and in the derivation of the Gibbs-Tetrode formula we have tacitly assumed quantization of the translational motions. In the latter case, while the quantum relation has been introduced in a way that is by no means explicit, nevertheless it is indispensable. Now, if the translational energy of a monatomic gas is to be quantized, we might suspect at once that the value $\frac{3}{2}R$ for C_v for monatomic gases is only a limiting value just as $C_v = 3R$ is a limiting value for monatomic solids. At some low temperature we should expect the equipartition law for monatomic gases to fail and the heat capacity to fall below the normal value. Indeed, Eucken[1] has obtained experimental confirmation of this degeneration in the case of helium, for which he finds values of C_v as low as 2.90 at low temperatures. It may very well be, of course, that his results are in error, but until they are so proven the problem cannot be regarded as

[1] *Ber. deut. physik. Ges.*, 18, 4 (1916).

academic. Indeed, the problem of gas degeneration has been considered by Sackur,[1] Tetrode,[2] Keesom,[3] Lenz and Sommerfeld,[4] Scherrer,[5] Planck,[6] and Nernst;[7] certainly an impressive array of investigators.

Most of these investigators attempted to formulate an expression for the heat capacity of an ideal gas at low temperatures by the method Debye used for the monatomic crystal. It requires enough stretch of our imagination to regard a crystal as a continuous homogeneous medium. To ascribe to an ideal gas the properties of such a medium is certainly a very artificial proceeding.

On the other hand, Scherrer and Planck attempted to quantize the motions of the individual molecule. They could not reach a complete solution because there is no such thing as an average gas molecule and we have no way of determining the actual motions. Nevertheless, the problem is one of great interest.

We shall scrutinize the use of the quantum relation in the formula for the entropy of a monatomic gas with the idea of attempting to set up the complete expression for the heat capacity. In our derivation of equation (85), it was assumed that the generalized space was divided into cells of the dimensions h^{3N}. h in turn is of the dimensions of momentum times length. Obviously these cells have faces which are of the area h. If we knew the extent in length of one of these faces, we would at once know the magnitude of the quantum of momentum for the particular molecule in this degree of freedom. Thus, we see that it is the momentum of a gas molecule and not the energy which is quantized. For each molecule in each degree of freedom there is some length l which determines the unit by which it can change its momentum. Apparently all we can hope to do is to calculate a sort of average $\bar{l}$ for the gas: the actual values of l must vary widely. Now since the value of the quantum of momentum will certainly not depend upon the shape or size (within limits) of the containing vessel, we can assume that this average value $\bar{l}$ must be independent of these factors. Dimensional considerations would suggest that $\bar{l}$ is a function of $\frac{V}{N}$, the average volume per molecule. At first thought we might think that the actual l is the mean free path of the gas. But the mean free path depends upon the effective diameter of the molecules and the data for the entropy of monatomic gases certainly do not indicate that effective diameter has anything to do with the case.[8]

[1] *Ann. Physik.*, (4) **40**, 67 (1913).

[2] *Phys. Z.*, **14**, 212 (1913).

[3] *Phys. Z.*, **15**, 695 (1914).

[4] Sommerfeld, Vorträge über die kinetische Theorie der Materie und der Electrizität. Wolfskehl-Kongress in Gottingen, p. 125, Teubner, Berlin, 1914.

[5] Göttinger Nachr., **8**, July, 1916.

[6] *Ann. Physik.*, (4) **50**, 385 (1916).

[7] Die theoretischen und experimentallen Grundlagen des neuen Wärmesatzes, p. 154, Halle, 1918.

[8] It should be noted that mean free path as calculated by ordinary probability may not be significant. If the generalized space is really a network, the effective diameter may have nothing to do with the probability of one molecule's colliding with another molecule.

We might assume that

$$\bar{l} = f\left(\frac{V}{N}\right)^{1/3},$$

apparently the simplest assumption that we can make. That $\bar{l}$ should be exactly equal to $\left(\frac{V}{N}\right)^{1/3}$ seems very improbable. A much more reasonable assumption is that

$$\bar{l} = K\left(\frac{V}{N}\right)^{1/3}, \tag{107}$$

where K is a constant.

Let us proceed on this assumption. We would have for the average momentum of a molecule in any degree of freedom

$$mV = \frac{nh}{K\left(\frac{V}{N}\right)^{1/3}}, \tag{108}$$

where $\frac{h}{K\left(\frac{V}{N}\right)^{1/3}}$ is the fundamental quantum of momentum. The energy quantum will not be constant since the energy is proportional to the square of the momentum

$$\epsilon = \tfrac{1}{2}mV^2 = \frac{n^2h^2}{2mK'\left(\frac{V}{N}\right)^{2/3}} = n^2\epsilon_0, \tag{109}$$

where

$$\epsilon_0 = \frac{h^2}{2mK'\left(\frac{V}{N}\right)^{2/3}}. \tag{110}$$

The quantized distribution law for a monatomic gas now becomes

$$N_n = Ke^{-n^2\epsilon_0/kT}, \tag{111}$$

which is quite different from the law for a monatomic solid (42). The total energy of the gas by (45) will be given by the expression

$$E = 3N\frac{\Sigma n^2\epsilon_0 e^{-n^2\epsilon_0/kT}}{\Sigma e^{-n^2\epsilon_0/kT}}.$$

Let us call the series of the numerator Σ_2 and of the denominator Σ_1. We then have

$$C_v = \frac{dE}{dT} = 3N\frac{d\left(\frac{\Sigma_2}{\Sigma_1}\right)}{dT}. \tag{112}$$

For the entropy,

$$\int_0^T \frac{C_v dT}{T} = \int_0^T \frac{3N}{T} \frac{d\left(\frac{\Sigma_2}{\Sigma_1}\right)}{dT} dT. \tag{113}$$

This may be integrated by parts,

$$3N \int_0^T \frac{d\left(\frac{\Sigma_2}{\Sigma_1}\right)}{dT} \frac{dT}{T} = \frac{3N\Sigma_2}{T\Sigma_1} + \int_0^T \frac{\Sigma_2}{\Sigma_1} \frac{dT}{T^2}.$$

Now inspection shows that

$$\frac{d\Sigma_1}{dT} = \frac{\Sigma_2}{kT^2},$$

so that the last integral above becomes

$$kln\Sigma_1,$$

since at 0° K., $\Sigma_2 = 0$, $\Sigma_1 = 1$. The increase in entropy from absolute zero to any given temperature T is then given by the expression

$$\int_0^T dS = \frac{3N\Sigma_2}{T\Sigma_1} + 3Nkln\Sigma_1. \tag{114}$$

It remains to evaluate the series. If we multiply Σ_1 by $\sqrt{\frac{\epsilon_0}{kT}}$, we have

$$\Sigma_1 \sqrt{\frac{\epsilon_0}{kT}} = \sqrt{\frac{\epsilon_0}{kT}} + e^{-\epsilon_0/kT} \sqrt{\frac{\epsilon_0}{kT}} + e^{-4\epsilon_0/kT} \sqrt{\frac{\epsilon_0}{kT}} + \cdots.$$

At high temperatures $\sqrt{\frac{\epsilon_0}{kT}}$ becomes small and we approach as a limit the integral

$$\int_0^\infty e^{-X^2} dX = \frac{\sqrt{\pi}}{2}.$$

Hence at high temperatures

$$\Sigma_1 = \frac{1}{2}\sqrt{\frac{\pi kT}{\epsilon_0}}, \qquad \Sigma_2 = kT^2 \frac{d\Sigma_1}{dT} = \frac{(kT)^{3/2}\sqrt{\pi}}{4\sqrt{\epsilon_0}}.$$

We then have from (110) and (114)

$$\int_0^T dS = \frac{3Nk}{2} + Nkln \frac{(2\pi mkT)^{3/2}}{h^3} \frac{V}{N} + 3NklnK. \tag{115}$$

But this expression differs from the Gibbs-Tetrode expression for the entropy of a monatomic gas only by a constant. If we set $ln\frac{K}{2} = \frac{1}{3}$, the two expressions

become identical. This indicates that the entropy of an ideal gas at absolute zero differs from zero only by a dimensionless constant. Of course, actual gases liquefy before we reach the absolute zero. It appears possible, however, to cool helium at constant volume and low pressure so near to zero that the integral

$$\int_0^T C_v d\ln T$$

would be negligible if the theory of degeneration is correct. If the entropy of a gas is different from zero at 0° K., we should expect it to depend upon the volume and not upon a dimensionless constant.

Since the theory of degeneration indicates that the heat capacity of an ideal gas falls to 0 at absolute zero, it is interesting to obtain the curve for C_v as a function of the temperature. At high temperatures, of course, equation (112) gives a value for C_v of $\frac{3}{2}R$. At low temperatures we must evaluate the series of (112) term by term, which is a somewhat laborious process. The curve obtained for C_v resembles, at low temperatures, the curve (I), Fig. 12, given by Reiche's equation for rotational heat capacities. This is not surprising, since equation (112) resembles the equation obtained by Reiche in form. The maximum of the curve occurs at a value of $\frac{\epsilon_0}{kT}$ equal to about 2.2. We must of course recognize that we are doing here for a gas what we do when we try to represent the heat capacity of a monatomic solid by the Einstein equation. We are assuming a single average frequency whereas there are an innumerable number of different frequencies. Reasoning by analogy then, we might predict that C_v for an actual gas would resemble in form somewhat the regular curve for a monatomic solid and would fall to zero at absolute zero. The maxima and minima of different frequencies would overlap in such a way that the resulting curve would be free from either, rising monotonously to an asymptotic value of $\frac{3}{2}R$. We should expect the actual curve to show deviations from the $\frac{3}{2}R$ value at temperatures where $\frac{\epsilon_0}{kT} = 1$. We can calculate ϵ_0 by equation (110). For a concentration of 30 mols. of helium per liter for which Eucken found $C_v = 2.90$ calories at 18° K., we find that $\frac{\epsilon_0}{kT} = 1$ at about 5° K. This agrees with Eucken's results, assuming of course that Eucken's low results are of significance and not due to experimental error.

At any rate, it appears likely that if C_v could be measured experimentally for helium to a very low temperature, the integral

$$\int_0^T C_v d\ln T$$

would be found very nearly equal to the entropy of the gas at the temperature T. This agrees with the result we should expect from a consideration of thermodynamic probability. We have seen that thermodynamic probability, as

we have used it, appears to be concerned only with the distribution of momentum, not with the arrangement of the molecules in space.[1] According to this view, the thermodynamic probability must become small as the temperature approaches zero, unless of course we admit the existence of zero temperature energy. Now, if the entropy of an ideal gas be zero at absolute zero, what about solutions and supercooled liquids? Surely these states of matter are intermediate between gases and solids.

For these also we can say that the thermodynamic probability certainly becomes small as we approach 0° K., again assuming the absence of all kinetic energy at absolute zero. The existence of zero temperature energy such as has been suggested by Planck might alter the situation. But, it does not follow that the integral

$$\int_0^T C_p d\ln T$$

will bring the entropy to zero. Planck [2] is of the opinion that thermodynamic relations cease to be valid near the absolute zero. When we differentiate the entropy to obtain the relation

$$\frac{dS}{dT} = \frac{C_p}{T},$$

we assume that the entropy is a continuous function of the temperature. But, by the quantum theory, the thermodynamic probability, and hence the entropy, are not continuous functions of the temperature, and, at low temperatures, the discontinuity becomes significant. Gibbs pointed out that the laws of thermodynamics are generalizations from statistical mechanics which are true when the number of degrees of freedom is large. At low temperatures matter behaves as though it had lost degrees of freedom.

The question of course is highly academic. From the practical standpoint, as Lewis and Gibson have pointed out, the behavior of the heat capacities of supercooled liquids is very anomalous. Even if the integral

$$\int_0^T C_p d\ln T$$

does bring the entropy to zero at 0° K., we shall probably not be able to determine C_p at temperatures low enough to prove it.

The Statistical Basis of Thermodynamics

We have, in equation (114), an expression for the integral

$$\int_0^T \frac{1}{T}\frac{dE}{dT}dT = \int_0^T C_v d\ln T = \int_0^T dS = \frac{N\Sigma\epsilon_n e^{-\epsilon_n/kT}}{T\Sigma e^{-\epsilon_n/kT}} + Nk\ln\Sigma e^{-\epsilon_n/kT},$$

[1] Compare Lewis and Gibson, *J. Am. Chem. Soc.*, **42**, 1532 (1920).

[2] Wärmestrahlung, 4th edition, p. 218, Barth, Leipzig, 1921.

where N is the total number of degrees of freedom. This expression was obtained by differentiating the general equation (45) for the total energy of a system in which the energy is quantized, and integrating with respect to $dlnT$. $\Sigma\epsilon_n e^{-\epsilon_n/kT}$ and $\Sigma e^{-\epsilon_n/kT}$ are then general series arising from any form of a quantized distribution law. These equations should then be applicable to all forms of matter.

If there is no arbitrary constant in the entropy, then

$$S = \frac{N\Sigma\epsilon_n e^{-\epsilon_n/kT}}{T\Sigma e^{-\epsilon_n/kT}} + Nkln\Sigma e^{-\epsilon_n/kT},$$

and by (45)

$$E = \frac{N\Sigma\epsilon_n e^{-\epsilon_n/kT}}{\Sigma e^{-\epsilon_n/kT}}.$$

Hence

$$S = \frac{E}{T} + Nkln\Sigma e^{-\epsilon_n/kT}. \tag{116}$$

But the right hand side of (116) is the logarithm of the thermodynamic probability multiplied by k. This may be demonstrated in various ways but perhaps most easily by the method of Planck.[1] By the quantum distribution law (42), the number of molecules having the energy ϵ_n is

$$N_n = Ke^{-\epsilon_n/kT}.$$

If the total number of molecules is N, then the thermodynamic probability is equal to the number of different ways in which these molecules may be arranged to give the distribution required by (42), and this number is given by the expression

$$P = \frac{N!}{N_0!\, N_1!\, N_2 \cdots}. \tag{117}$$

But since $n! = n^n e^{-n}$ when n is large, the expression above becomes

$$P = \frac{N^N e^{-N}}{N_0^{N_0} N_1^{N_1} \cdots e^{-N_0} e^{-N_1}}.$$

Since

$$N = N_0 + N_1 + N_2 + \cdots,$$

we have

$$P = \left(\frac{N}{N_0}\right)^{N_0}\left(\frac{N}{N_1}\right)^{N_1}\left(\frac{N}{N_2}\right)^{N_2}\cdots. \tag{118}$$

Writing

$$S = klnP = -kln\frac{1}{P},$$

[1] Planck, Würmestrahlung, 4th edition, p. 123, Barth, Leipzig, 1921.

we get from (118)

$$S = -Nk\Sigma\left(\frac{N_n}{N}\right)ln\left(\frac{N_n}{N}\right). \tag{119}$$

But since

$$\frac{N_n}{N} = K'e^{-\epsilon_n/kT}$$

and

$$K'\Sigma e^{-\epsilon_n/kT} = 1,$$

we may write

$$S = -Nk\Sigma\left(\frac{N_n}{N}\right)\left(lnK' - \frac{\epsilon_n}{kT}\right). \tag{120}$$

But

$$E = \Sigma N_n\epsilon_n$$

and

$$\Sigma\left(\frac{N_n}{N}\right) = 1,$$

so that

$$S = \frac{E}{T} + Nkln\Sigma e^{-\epsilon_n/kT},$$

which is identical with (116) above.

The integral $\int_0^T C_v dlnT$ is equal to the logarithm of the thermodynamic probability multiplied by R. We have, therefore, established the relation between energy, temperature and entropy by statistical mechanics, for the general case of a system in which the energy is quantized. All other thermodynamic functions may be defined in terms of the energy, temperature and entropy.

CHAPTER XVIII

PHOTOCHEMISTRY

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Photochemical reactions are produced when a reaction system is "illuminated," that is to say when the system receives from an external source radiation of a frequency which is practically non-existent in the radiation of the system itself. The science of photochemistry hitherto has been concerned more especially with the reactions caused by the light of the visible and ultra-violet spectrum. This represents but a small fraction of the electromagnetic waves now known to be emitted by vibrating particles. There has recently developed a tendency to widen the scope of the study of reactions brought about by radiations from without the reaction system to include all varieties of wave motions. Eventually, it is to be hoped, a general treatment for all such reactions will be available. As yet, only the beginnings of such a general treatment can be given. In the present chapter the theoretical principles involved in the utilization of visible and ultra-violet radiation as an auxiliary to chemical change will be discussed. The technique of work in the infra-red region and the effect of such vibrations in chemical processes are treated elsewhere. The scope of the subject as far as the light is concerned may be judged from the following table which gives the region, the wave-lengths and frequencies of the various electro-magnetic radiations now known.

TABLE I

Region	Wave-lengths in Ångstrom Units	Frequencies
X-rays	1–510 Å.	3×10^{18}–5.9×10^{15}
Ultraviolet	510–4000 Å.	5.9×10^{15}–7.5×10^{14}
Visible	4000–8000 Å.	7.5×10^{14}–3.75×10^{14}
Infra-red	8000–3.14×10^{6} Å.	3.75×10^{14}–9.55×10^{11}
Hertzian electric	10^{7}–10^{13} Å.	3×10^{11}–3×10^{5}

When light falls on any body the incident energy may suffer various changes. A portion is generally reflected, a further portion absorbed and the residue transmitted. The amounts of the incident light which take part in these several processes vary relatively to one another, depending on the wave-length of the light and on the nature of the body upon which the light impinges. The total incident light energy must, however, by the law of conservation of energy, be equal to the sum of the energies of the light reflected, absorbed and

transmitted. It is with the light which is absorbed from the incident radiation that the science of photochemistry is concerned. This fact is embodied in the first law of photochemistry.

The Grotthus-Draper Photochemical Absorption Law: Grotthus, in 1818, enunciated the fundamental principle underlying all processes of photochemical change in the statement that: *Only the rays that are absorbed are effective in producing chemical change.* Grotthus's statement was based upon theoretical considerations alone. Its importance became recognized when stated anew by J. W. Draper,[1] as a deduction from investigations of the photochemical reaction between hydrogen and chlorine. "This quality gained by chlorine arises from its having absorbed thitonic rays, corresponding in refrangibility to the indigo."

Not all absorbed radiation results in chemical change. The numerous investigations of spectroscopy demonstrate the occurrence of absorption of light in many cases entirely unassociated with chemical change. In such case, the light suffers a transformation into one or other forms of radiant energy or into change in the energy content of the molecules, which change, however, need not result in chemical reaction. Photochemical change is, therefore, one possible resultant of the absorption of radiation. Furthermore, as will be more fully discussed in the sections dealing with photosensitization, it is not necessary that the reacting species absorb the radiation. Photo-reactions may result from the absorption of light by one of the non-reactive constituents of the system.

The quantitative formulation of the Grotthus-Draper principle may be derived from the quantitative laws of absorption.

Fresnel's Law of Reflection: The proportion of incident monochromatic light reflected by a surface perpendicular to the incident beam is given by the expression

$$I_r = \left(\frac{n-1}{n+1}\right)^2 I_0,$$

where I_0 is the incident light, I_r the reflected light, n the refractive index of the reflecting medium for light of the wave-length employed. Since n is a constant for a given medium and given wave-length, it follows that

$$I_r = RI_0,$$

where R is a proportionality factor connecting the two magnitudes. From this equation it follows that the light penetrating the medium under the above circumstanes is given by the expression

$$I_0 - I_r = I = I_0(1 - R).$$

The quantity of this light, I, which is absorbed by the medium, is given by two laws of absorption, one for pure substances, one for solutions.

[1] *Phil. Mag.*, (3) **19**, 195 (1841); **23**, 401 (1843); **27**, 327 (1845).

Lambert's Absorption Law: Equal proportions of the penetrating radiation are absorbed by layers of equal thicknesses of a homogeneous absorbing medium. In other words, if I is the penetrating radiation, and I_d the radiation transmitted by a layer of depth d, the relationship between these two magnitudes is given by the expression

$$I_d = Ie^{-kd}.$$

The constant, k, is the absorption coefficient of the substance for the light employed and is dependent, not only on the nature of the medium, but also on the wave-length of the light employed. The law obviously associates the absorptive power with the number of molecules present. In equal layers, equal numbers of molecules absorb equal fractions of the penetrating radiation. When applied to solutions of an absorbing body in a non-absorbing or diactinic solvent, it is evident that the expression must be modified to indicate the molecular concentration.

Beer's Law: The absorption of light by solutions depends upon the thickness, d, of the layer traversed and on the molecular concentration, c, in that layer,

$$I_d = I \cdot e^{-k'cd}.$$

The constant, k', is, in this case, the molecular absorption coefficient. Beer's law has been tested and found to be valid in many cases. Exceptions are, however, known. It is obvious that in many solutions difficulty will arise in expressing the magnitude of the concentration of the absorbing species.

For media obeying Beer's Law, it is evident that the absorbed light is given by the expression

$$I - I_d = I(1 - e^{-k'cd}).$$

The principle embodied in the Grotthus-Draper absorption law would therefore be expressed mathematically by the equation

$$\frac{dc}{dt} = kI(1 - e^{-k'cd}),$$

where k is a proportionality factor connecting the rate of change, $\frac{dc}{dt}$, with the energy absorbed by a layer of thickness d. It must be emphasized anew that all these laws of absorption apply only to monochromatic radiation. The equation given represents the simplest possible relationship between absorbed light and photochemical reactions; it was found to be approximately obeyed by Wittwer [1] in his researches on the photochemical interaction of dissolved chlorine with water. It will be shown that many factors may operate to produce deviations from this simple law connecting absorption and extent of reaction.

[1] *Pogg. Ann.*, **94**, 597 (1855); **96**, 373 (1855); **97**, 304 (1855).

Actinometry: It is upon an assumption of such a proportionality between chemical reaction and intensity of absorbed light that all actinometers are based. The light is measured by measurement of the chemical reaction produced. Draper [1] used the rate of hydrogen and chlorine combination as an actinometer. Bunsen and Roscoe in their classical researches [2] on the same reaction considerably improved the technique of the measurement.

The gases were contained in a suitable vessel with parallel plane faces and were stored over water saturated with the gas mixture. Measurement of the contraction occurring on solution of the hydrogen chloride formed by the reaction was made in a horizontal capillary with attached scale, the meniscus being formed by a thread of water. The displacement of this thread of liquid was governed by the intensity of the illumination and the diameter of the capillary tube; so that, by making this latter narrow, a large displacement of the meniscus could be effected by even weak illumination.

Bunsen and Roscoe concluded that the ordinary laws of optics were obeyed, in that they found (1) that the reaction occurring was inversely proportional to the square of the distance from the source of illumination, (2) that the laws of reflection and absorption were likewise applicable. Many modifications of the Bunsen-Roscoe actinometer have since been employed. A specially refined form was used by Burgess and Chapman [3] in their investigations of the hydrogen-chlorine combination. It should also be observed that recent work by Baly and Barker [4] has indicated that the rate of reaction increases more rapidly than the relative intensity, when this latter is widely varied. The significance of this in modern photochemical theory will be discussed later. It is evident, however, that such a conclusion depreciates the value of the reaction for actinometric purposes.

Bunsen and Roscoe studied also the silver-chloride actinometer determining the time required by light of a given intensity to darken photographic paper to a standard tint. As is well known, numerous applications of this actinometer have been employed in photographic work.

The photosensitive reaction between mercuric chloride and ammonium oxalate,

$$2HgCl_2 + (NH_4)_2C_2O_4 = Hg_2Cl_2 + 2CO_2 + 2NH_4Cl,$$

has also been employed. The carbon dioxide evolved may be determined or the mercurous chloride weighed.

Photoelectric cells have been used for actinometric purposes. Rigollot,[5] utilizing the photoactivity of oxidized copper plates in alkali halide solutions, determined the light intensity from the strength of current produced when one plate was illuminated.[6]

[1] *Loc. cit.*

[2] *Pogg. Ann.*, **96**, 373 (1855); **100**, 32, 481 (1857); **101**, 193 (1859); *Ostwald's Klassiker*, Nr. **34** and **38**.

[3] *J. Chem. Soc.*, **89**, 1402 (1906).

[4] *J. Chem. Soc.*, **119**, 653 (1921).

[5] *J. Phys.*, **6**, 520 (1897).

[6] For the theory of this process, see Goldmann, *Ann. Physik.*, (4) **44**, 901 (1914); Garrison, *J. Phys. Chem.*, **27**, 601 (1923).

It is important to emphasize that such actinometers have little applicability in exact modern scientific photochemistry. They are essentially individual instruments and measure relative light intensity only for the particular reaction involved in the actinometric process or for reactions closely similar to the actinometric reaction. This is evident when we remember the Grotthus-Draper principle and the widely varying absorptive capacities of different reaction systems. For a given system, even, the chemical actinometer is only strictly applicable with monochromatic radiation. With a whole spectrum of light, the reaction will not be proportional to the intensity. For, the photochemical effect of varying wave-lengths and the extent of absorption vary enormously. In general, the ultra-violet region is much more efficient photochemically than the visible region.

The technique of all modern photochemical investigation, correlating light energy with chemical energy produced, involves actual physical measurement of the energy of the incident radiation, of the fractions reflected and absorbed. Thermocouple-galvanometer systems are employed, calibrated against standard candle-power sources. Monochromatic radiation is employed as far as practicable, this being attained by the use of suitable light filters with arc, filament or mercury-vapor lamp sources. Recently, an abundant literature of such technique has been forthcoming.[1]

The Energetics of Photochemical Processes

The reactions produced by the agency of light include both reactions occurring with a free energy decrease and those in which the direction of change is opposed to the normal operation of the chemical forces of the system, in which, therefore, a free energy increase occurs. In the former, the normal, "dark," or purely thermal reaction is promoted by the agency of the light, which therefore acts somewhat as does a catalyst. The hydrogen-chlorine reaction is the best known example of such a process accompanied by free energy decrease. The gases, quite stable at ordinary temperatures in the dark, may react with explosive violence when suitably illuminated. The end-product, however, of both the thermal and photochemical reaction is hydrogen chloride. It is evident that, in such reactions, small amounts of light energy may be effective in producing large amounts of chemical change, the light providing the starting mechanism of the normal chemical process.

Of photo-reactions in opposition to the normal chemical forces, accompanied, therefore, by a free energy increase, the most important reaction is that occurring in the plant kingdom, where carbon dioxide and water are converted, in sunlight, into complex organic molecules. In such photo-synthesis, free energy is accumulated. It is evident that, since the law of conservation

[1] Warburg, *Sitz.-ber. preuss. Akad.*, 746 (1911); 216 (1912); 644 (1913); 872 (1914); 230 (1915); 314 (1916); 300, 1228 (1918); 960 (1919). Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921). Noddack, *Z. Elektrochem.*, **27**, 359 (1921). Eggert and Noddack, *Sitz.-ber. preuss. Akad.*, **39**, 631 (1921); 116 (1923). Bonhoeffer, *Z. Physik*, **13**, 94 (1923). Grüss, *Z. Elektrochem.*, **29**, 144 (1923).

of energy must be fulfilled, comparatively large amounts of light energy must be consumed in such processes. It appears that the efficiency of utilization of light energy by green leaves to produce chemical energy is practically ideal.[1] Reactions simpler in nature and readily susceptible to laboratory investigation are also known. The ozonization of oxygen, the decomposition of ammonia and of hydrogen chloride, the polymerization of anthracene to dianthracene are photo-reactions opposed to the normal free-energy factors of the reaction system.

The relationships existing between light energy consumption and chemical energy produced were investigated in the era of photochemistry prior to the establishment of the quantum theory by determining the number of calories absorbed by the reacting system and comparing this with the energy change accompanying the chemical process as determined from ordinary calorimetric data. With the application of quantum concepts to molecular processes a new method of approach was possible, as was indicated by Einstein in 1905, and developed by him more particularly in 1912 [2] and 1916.

Law of the Photochemical Equivalent: Einstein assumes that the occurrence of a photochemical reaction is to be ascribed to the absorption of quanta of radiation, each single molecule requiring one quantum, $h\nu$, of a frequency, ν, characteristic of the absorbing molecule. The absorption of a quantum of radiation becomes, on such assumptions, the primary stage in a photochemical reaction. It is evident that this concept brings about a parallelism between the reactions of photochemistry and the phenomena of the photoelectric effect and the existence of the stationary states of the atom as involved in the Bohr theory of the atom and of spectral series. It will be realized, however, that the application of quantum concepts in the two latter phenomena will, in general, be simpler than in the case of photochemical reaction; for, with photochemical processes, it is only the primary process which will involve the simple quantum relationship. This primary process may be succeeded by further processes, initiated by the quantum process, to yield the net observed photo-reaction. The secondary processes will, in general, be entirely independent of the light action. They may be so considerable as to mask almost completely the energy change inherent in the primary quantum absorption, which alone will be governed by the nature and intensity factors of the light absorbed.

The Einstein concept of the initiation of photo-reactions has given an entirely new orientation to the investigations of photochemical theory. Recent studies are concerned almost entirely with the agreement or disagreement between actual experiment and the demands of the law of the photochemical equivalent. The classic researches of the earlier days of photochemistry, admirably summarized by Weigert,[3] are being reinvestigated in

[1] Weigert, Die chemischen Wirkungen des Lichts, p. 106, Stuttgart, 1911.

[2] *Ann. Physik.*, [4] **37**, 832 (1912); *Verh. deut. physik. Ges.*, **18**, 315 (1916). See also Weigert, *Z. Physik*, **14**, 383 (1923); also, Chapter XVI.

[3] Die chemischen Wirkungen des Lichts, Stuttgart, 1911.

order to ascertain the extent to which the equivalent law is obeyed, to seek, on the basis of quantum relationships, the mechanism of photochemical changes. Marked progress has already been achieved and a broad field for future investigation has been revealed.

We may examine the energy, U, obtained in the absorption by a gram molecule of an absorbing reactant, when each molecule receives a quantum, $h\nu$, of frequency ν. The relationship existing is

$$U = Nh\nu,$$

where N is the Avogadro constant. The following table gives the magnitude of $h\nu$ in ergs and of U in calories for several typical wave-lengths in the visible and ultraviolet spectrum.

TABLE II

ENERGY CORRESPONDING TO VARIOUS WAVE-LENGTHS OF LIGHT

Color of Light	Wave-length in Ångstroms	$h\nu$	$U = Nh\nu$
Red	7500–6500	$2.62\text{–}3.02 \times 10^{-12}$	37,800–43,630
Orange	6500–5900	$3.02\text{–}3.33 \times 10^{-12}$	43,630–48,060
Yellow	5900–5750	$3.33\text{–}3.42 \times 10^{-12}$	48,060–49,320
Green	5750–4900	$3.42\text{–}4.01 \times 10^{-12}$	49,320–57,880
Blue	4900–4550	$4.01\text{–}4.32 \times 10^{-12}$	57,880–62,330
Violet	4550–3950	$4.32\text{–}4.97 \times 10^{-12}$	62,330–71,800
Ultraviolet	2000	9.9×10^{-12}	142,000

It is at once evident that the absorption of light brings to a reaction system considerable energy quantities, whereby secondary processes of change may be secured. The table shows, qualitatively at least, why, in general, photoreactions are more frequently initiated by ultraviolet light than by visible light. Energy is accumulated in larger units with the shorter wave-lengths of light.

An example of the mode of calculation of the approximate relationship between quanta of light energy absorbed and number of molecules reacting may be given from a paper by Bodenstein,[1] who first gave a comprehensive analysis of existing data on the basis of the quantum relationship. The calculation on the anthracene—dianthracene polymerization, studied by Luther and Weigert,[2] may be reproduced.

Luther and Weigert found that, in 1 cc. of solution illuminated for 1 second over an area of 1 sq. cm. at a distance of 1 cm. from the light source, the amount of anthracene polymerized amounted to between 3×10^{-7} and 5×10^{-7} mols., or, in the mean, $4 \times 10^{-7} \times 6 \times 10^{23} = 2.4 \times 10^{17}$ molecules of anthracene polymerized per second. The arc lamp used consumed 8.8 amperes at 53 volts or 470 watts. Bodenstein estimated from the experimental data that 1/500 of the light is efficient and that 1/13 of this falls upon the square centimeter of surface illu-

[1] *Z. physik. Chem.*, **85**, 329 (1913).

[2] *Z. physik. Chem.*, **51**, 297 (1905); **53**, 385 (1905).

minated. Expressing this energy quantity in ergs and dividing by the quantum of the absorbed frequency, expressed in ergs, 5×10^{-12}, one obtains the number of quanta involved, thus

$$\frac{470 \times 0.29 \times 42 \times 10^6}{500 \times 13} \times \frac{1}{5 \times 10^{-12}} = 2 \times 10^{17} h\nu.$$

It is evident therefore that in this case there is an approximate equality between quanta absorbed and molecules reacting. Further data of Weigert [1] confirm this calculation.

Some of the data obtained by Bodenstein in this survey are reproduced in the following table.

TABLE III

RELATION BETWEEN QUANTA ABSORBED AND MOLECULES REACTING

Reaction	Molecules/$h\nu$
$3O_2 = 2O_3$	$1h\nu$ per $2O_3$
$2NH_3 = N_2 + 3H_2$	$4h\nu$ per NH_3
Anthracene → Dianthracene	1–$3h\nu$ per $C_{14}H_{10}$
o-$C_6H_4NO_2CHO \rightarrow C_6H_4NOCOOH$	$9h\nu$ per molecule
$2O_3 + Cl_2 = 3O_2 + Cl_2$	1
$H_2 + Cl_2 = 2HCl$	10^6
$2O_3 = 3O_2$	100–1000
$CH_3COCH_3 + H_2O = CH_4 + CH_3COOH$	200
$2H_2O_2 = 2H_2O + O_2$	100
Oxidation of Quinine	1–200
$CO + Cl_2 = COCl_2$	100
$Br + C_7H_8 = HBr + C_7H_7Br$	10^6

A glance at the data in the second column reveals that, while some cases of equivalence are obtained, there are some striking deviations. Especially noticeable is the case of the hydrogen-chlorine combination in which approximately 10^6 molecules of chlorine react, in a sensitive gas mixture, for every quantum of light energy absorbed. The divergence led Bodenstein to a theory of photochemical reaction which has proved exceedingly stimulating to the science. We shall trace the ensuing developments in an account of the quantitative examination of the law of the photochemical equivalent. Exact measurements, with practically monochromatic radiation, in a number of reactions have been carried out by Warburg. Other determinations have been supplied from the laboratories of Nernst, Weigert and Bodenstein.

The Ozonization of Oxygen: This reaction is accompanied by a free energy increase. Lenard showed [2] that the ozonization could be effected by short wave-length light of 1850 Å. Goldstein found [3] that in the region 1200–2000 Å. ozonization occurs, whereas between 2300 and 2800 Å. the reverse reaction predominates. Lenard showed that short wave-length light would produce both ionization and ozonization but that the two phenomena were independent.

[1] *Ber.*, **42**, 858 (1909).
[2] *Ann. Physik.*, 1, 480 (1900).
[3] *Ber.*, **36**, 3042 (1913).

This condition is not always fulfilled. Thus, in the case of ammonia decomposition,

$$N_2 + 3H_2 = 2NH_3 + 22{,}000 \text{ cals.},$$
$$6H = 3H_2 + 297{,}000 \text{ cals.},$$
$$2N = N_2 + x \text{ cals.}$$

Whence

$$N + 3H = NH_3 + \frac{319{,}000 + x}{2} \text{ cals.},$$

where x = the heat of dissociation of nitrogen into atoms. It is apparent that this energy quantity is greater than that derivable from an energy quantum at a wave-length $\lambda = 2090$ Å., namely 135,900 cals. The same is true in the case of the ozonization of oxygen at the wave-length, $\lambda = 2530$ Å. The dissociation of oxygen into atoms requires more than 136,000 calories whereas the energy quantum amounts only to 112,000 calories per mol. at the stated frequency.

Warburg seeks, in this deficit of quantum energy, an explanation of the yield, less than would correspond to the equivalent law, for ammonia decomposition and for ozonization at the higher wave-length. He would anticipate lesser yields than the law of the equivalent demands in all such cases. Instead therefore of a simple mechanism,

$$O_2 + h\nu = 2O,$$
$$O_2 + O = O_3,$$

Warburg would substitute a mechanism

$$O_2 + h\nu = O_2(h\nu),$$
$$O_2(h\nu) + O_2 = O_3 + O,$$

or

$$O_2(h\nu) + 2O_2 = 2O_3,$$

the energy-rich oxygen molecule producing ozone by collision with normal molecules. The deficit in yield would then be attributed to loss, by radiation of energy, from the energy-rich molecule before a favorable collision occurred.

Upon investigating reaction systems in solution as opposed to gas reactions, Warburg found that even in cases where $Nh\nu$ was greater than the heat change accompanying the process the photochemical yield was less than the theory of the equivalence demands. This was true in the investigation of nitrite formation in solutions of potassium nitrate when illuminated by ultraviolet light.[1] Warburg suggests that the absorbed quantum is dissipated in the act of absorption.

Warburg has given [2] the following tabulation of his results for the several reactions studied at various wave-lengths.

[1] *Sitz.-ber. preuss. Akad.*, 1228 (1918). See, also, Anderson, *J. Am. Chem. Soc.*, **46**, 797 (1924)

[2] *Z. Elektrochem.*, 26, 54 (1920).

TABLE V

WARBURG'S EXPERIMENTAL DATA ON EINSTEIN'S LAW

Reaction	Molecules per $h\nu$ for		
	λ = 2070 Å.	λ = 2530 Å.	λ = 2820 Å.
HI decomposition	2.099	2.104	2.105
HBr decomposition	2.105	2.10	
Ozonization of O_2 (p = 125 kg)	0.96	0.55	
Ozonization of O_2 (p = 300 kg)	0.78	0.29	
Ozone decomposition in He		0.85	
NH_3 decomposition	0.23		
KNO aq. decomposition	0.25		
Fumaric → Maleic, 0.01 N.	0.11	0.10	0.13
Maleic → Fumaric, 0.01 N.	0.03	0.04	0.03

Warburg regards the two last isomeric changes as purely chemical changes, following the absorption of a light quantum and entirely independent of the Einstein law.

In a recent study of the photo-decomposition of potassium permanganate solutions, Rideal and Norrish [1] have shown that at least two quanta of wavelength λ = 3128 Å. are involved in the decomposition of the permanganate ion. For every five quanta absorbed in the wave regions λ = 3650, 3128 and 2536 Å., a permanganate ion decomposes. These authors show that with sodium oxalate present the photo-efficiency of the permanganate decomposition is very considerably increased.

We may now turn to the case noted in Bodenstein's classification of photo-reactions in which abnormally great quantities of chemical energy result from the absorption of light quanta. The most interesting and thoroughly studied is the hydrogen-chlorine combination.

The Hydrogen-Chlorine Combination: As already pointed out, this reaction was used by Draper to illustrate the Grotthus-Draper law of photochemical absorption and by Bunsen and Roscoe to show the applicability of the laws of optics to photochemical systems. The exhaustive investigations of Bunsen and Roscoe have been many times repeated in the intervening time. Confirmation of many of their conclusions has been reached. In other points newer technique has led to divergent conclusions.

Induction: The phenomenon of the induction period, the slow attainment of a maximum reaction velocity some time after the initial moment of illumination, intensively studied by Bunsen and Roscoe as to characteristics, was elucidated for the most part by Chapman and Burgess [2] and Chapman and MacMahon.[3] They established that the period of retarded action was always

[1] *Proc. Roy. Soc.*, **103**, 342, 366 (1923).
[2] *J. Chem. Soc.*, **89**, 1402 (1906).
[3] *Ibid.*, **97**, 845 (1909).

conditioned by the presence of foreign substances in the containing liquid or on the walls of the glass vessels or introduced into the gas by passage through lubricated stop-cocks. The induction period was not a function of the oxygen content of the gas—this only retarded the reaction velocity but did not affect the length of the induction period. Oxidizing agents were shown to have little or no influence on the induction period, nitric acid, hydrogen peroxide and potassium permanganate being tried. The slightest traces of ammonia, however, prolonged the induction period enormously, and, with very small amounts, the period was proportional to the amount present. The compounds NCl_3, NOCl, ClO_2 and NO_2 similarly retarded the initial reaction enormously. Chlorine monoxide and nitrous oxide were innocuous, pointing to the operation of specific chemical reaction with the hydrogen-chlorine mixture or one of the constituents. Organic nitrogen compounds such as albumen behaved like ammonia. From the researches of Chapman and his co-workers, it is evident that, in the early period of illumination of a hydrogen-chlorine mixture, part of the light energy is consumed in removal, by chlorination, of various impurities present in the reaction vessel. The constant maximum velocity attained represents an equilibrium state in which the introduction, and removal by chlorination, of impurities, have attained equal rates. Obviously, if precautions be taken against introduction of impurities, and those originally in the reaction vessel be removed by illumination of the reaction system, induction due to these causes will not be observed. Burgess and Chapman demonstrated this in a quartz vessel. Bodenstein and Dux [1] showed the same at a later date. The elimination of induction *due to impurities* can be achieved by a careful attention to experimental detail. Baly and Barker have recently claimed [2] that complete removal of impurities does not eliminate entirely the induction period. In their view, which will be amplified in the subsequent discussion, the hydrogen chloride produced in the process acts as a source of energy for the reaction of further molecules of hydrogen and chlorine. As the quantity of hydrogen chloride produced per unit of time increases, the reaction should become faster and faster by increase in the transfer of such energy to reactant molecules; a stationary state would be attained when an equilibrium is established between loss of energy by radiation and transference to reactants on the one hand and energy yield by illumination and reaction on the other. It should be emphasized however, by way of caution, that the presence of minute quantities of impurities in the Baly-Barker reaction system would lead to experimental results of the type obtained by them, so that evidence for the correctness of their viewpoint as to energy transfer from resultants to reactants should be obtained from other sources. Weigert has suggested [3] that impurities may have influenced the Baly-Barker experimental results.

Weigert and Kellermann [4] have decisively demonstrated by experimental

[1] *Z. physik. Chem.*, **85**, 297 (1913).

[2] *J. Chem. Soc.*, **119**, 653 (1921).

[3] *Z. physik. Chem.*, **106**, 428 (1923).

[4] *Sitz.-ber. preuss. Akad.*, 315 (1922); *Z. Elektrochem.*, **28**, 456 (1922); *Z. physik. Chem.*, **107**, 1 (1923).

methods the existence of an induction period in the hydrogen-chlorine reaction, of much shorter duration, however, than those previously discovered. The hydrogen chloride produced on illumination from a momentary intense spark is not produced instantaneously but in an after-effect occurring approximately 1/100 second after illumination. The purer the gas mixture the larger the duration of the after effect. For such an effect to be observed it is evidently necessary that a hydrogen-chlorine mixture be illuminated, since Bodenstein and Taylor [1] showed that chlorine, mixed with hydrogen 1/1600 second after illumination of the chlorine, had quite lost its reactivity. This was also found by Vollmer [2] for a somewhat longer time interval between illumination of the chlorine and admixture with the hydrogen.

Kinetics: Most of the experimental work on this reaction has been performed with the Bunsen-Roscoe type of actinometer. It is not well suited to kinetic studies. Chapman and MacMahon (*loc. cit.*) used this type, however, to show that reaction velocity was inversely proportional to the oxygen concentration in the initial stages of the reaction. Bunsen and Roscoe showed proportionality between reaction velocity and intensity of light, the conclusion which Baly and Barker have called into question. Chapman and Underhill [3] sought to determine the influence of hydrogen concentration in such a vessel. They found that, at low hydrogen concentrations, the velocity rose enormously with increase in hydrogen concentration to a flat maximum. Bodenstein and Dux [4] studied the kinetics of the reaction thoroughly by abandoning the Bunsen-Roscoe method of study and substituting a manometric method of study. The progress of the reaction under illumination was followed by freezing, in liquid air, the residual chlorine and the hydrogen chloride formed during exposure to light, the partial pressure of the unused hydrogen being then measured at temperatures determined by means of an oxygen thermometer. With this method, the effect of varying concentrations of hydrogen, chlorine, oxygen, hydrogen chloride and water vapor was exhaustively studied. Their conclusions were:

(1) The combination of hydrogen and chlorine under the influence of light is a reaction of the second order, the velocity being proportional to the *square of the chlorine concentration.* Hydrogen is without influence so long as it is present to the extent of at least one quarter of the volume of chlorine. At smaller hydrogen concentrations the velocity decreases.

(2) The hydrochloric acid formed is without influence on the velocity.

(3) Water vapor within certain limits (0.004–2.3 mm.) is also without influence.

(4) Oxygen retards the reaction in such a way that the velocity at all stages of the combination is inversely proportional to the concentration of the oxygen.

It is obvious that the equation of reaction of the system may in such case be represented by the expression

$$+\frac{d[2HCl]}{dt} = k\frac{I_0[Cl_2]^2}{[O_2]},$$

[1] *Z. Elektrochem.*, **22**, 202 (1916).
[2] *Z. Elektrochem.*, **20**, 494 (1914).
[3] *J. Chem. Soc.*, **103**, 496 (1913).
[4] *Z. physik. Chem.*, **85**, 297 (1913).

where the quantities in brackets denote concentrations of gases, I_0 the light absorbed, put proportional to reaction rate in agreement with Bunsen-Roscoe, t the reaction time.

Chapman and Whiston [1] dispute the conclusions of Bodenstein and Dux as to the order of the reaction with respect to chlorine. Using the technique of Chapman and earlier co-workers, they find that, within wide limits, the rate of formation of hydrogen chloride is given with fairly close approximation by the expression

$$+\frac{d[2HCl]}{dt} = \frac{kI_0[Cl_2]}{[O_2]}$$

or, in other words, since $I_0[Cl_2]$ is proportional to the radiation absorbed per unit time, the hydrogen chloride formed is nearly directly proportional to the radiation absorbed, inversely proportional to the oxygen concentration. The experimental method of Chapman and Whiston was to study the relative sensitivity of the same reaction mixture at 1, 0.5 and 0.25 atm. respectively. They showed that at 1 and 0.5 atmospheres total pressure the sensitivity was the same, within experimental error, whether the gases were moist (usual Bunsen-Roscoe method conditions) or dry. In this latter case anhydrous copper sulphate was used as absorbent for the hydrogen chloride produced. At 0.25 atm. total pressure, decreased sensitivity was manifest. The authors ascribe this to loss of energy by active chlorine molecules before fruitful impacts with hydrogen occur. They ascribe Bodenstein and Dux's conclusions to the influence of gradual production of inhibitors in the reaction system during an experiment.

A more thorough study of the reaction kinetics has just been completed with the following conclusions.[2]

(1) The rate of combination of the hydrogen and chlorine, in mixtures of electrolytic hydrogen and chlorine and oxygen, is nearly independent of the pressure of the gas.

(2) In mixtures, in which the concentrations of the hydrogen and the oxygen are kept constant, the rate of combination is

(*a*) proportional to the first power of the concentration of the chlorine when the proportion of hydrogen is small;

(*b*) proportional to a power of the concentration of the chlorine between the first and the second when a moderate proportion of hydrogen is present;

(*c*) proportional to the square of the concentration of the chlorine when the proportion of chlorine is small and that of the hydrogen large.

(3) In mixtures, in which the concentrations of the chlorine and oxygen are kept constant, the rate of combination is

(*a*) proportional to the concentration of the hydrogen when the proportion of hydrogen is small;

[1] *J. Chem. Soc.*, **115**, 1264 (1919).

[2] M. C. C. Chapman, *J. Chem. Soc.*, **123**, 3062 (1923).

(*b*) inversely proportional to a power of the concentration of the hydrogen which is rather less than $\frac{1}{2}$ when the proportions of hydrogen and chlorine are moderate;

(*c*) inversely proportional to a power of the concentration of the hydrogen which is rather less than 1 when the proportion of chlorine is small.

(4) The rate of combination is independent of the concentration of the oxygen in mixtures in which the concentration of the hydrogen is very small; for all other mixtures, it is inversely proportional to the concentration of the oxygen. The results can be summarized by the formula

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{k_1[\mathrm{H_2}][\mathrm{Cl_2}]^2}{k_3[\mathrm{H_2}]^{2-x}[\mathrm{O_2}] + [\mathrm{Cl_2}]}.$$

It is also concluded that the observed inhibitive effects of oxygen and of hydrogen are not—as has been hitherto assumed—due to the direct and independent action of these gases, but to the joint agency of both.

The absence of influence of water vapor within the limits above mentioned does not extend to extremely dry gases. Baker [1] and, later, Mellor and Russell [2] showed that hydrogen and chlorine, when thoroughly dried over phosphorus pentoxide, only slowly reacted in bright sunlight. There was a possibility that in these experiments long drying over phosphorus pentoxide might have introduced some inhibitors, e.g., oxygen, into the reaction system, which would account for the retardation observed. This possibility has been eliminated by recent work of Tramm,[3] who, using modern low temperature technique for the drying of gases by liquefaction and fractional distillation, showed that a hydrogen-chlorine mixture so dried was inactive photochemically. The introduction of a small amount of water vapor made a mixture so dried normally photosensitive. The inertness of dried hydrogen-chlorine mixture is confined, however, to the visible and near-ultraviolet region of the spectrum. Coehn and Jung have recently shown [4] that a dry mixture, quite inert to daylight for 20 days or to illumination for 10 minutes at 15 cm. distance from a 100-candle-power osram lamp, is quantitatively converted to hydrogen chloride when exposed for 12 minutes at 20 cm. distance from a quartz mercury vapor lamp. A screen of uviol glass, whose transmission extends to 2540 Å., was sufficient to protect the reaction mixture in a quartz tube from reaction. It is evident, therefore, that the wave-length active in causing the combination of a dried hydrogen-chlorine mixture lies between 2200 and 2540 Å.

Energetics: The reaction is one which shows large deviation from the Einstein law of photochemical equivalence. Bodenstein's calculation [5] may be reproduced.

[1] *J. Chem. Soc.*, **65**, 611 (1894).
[2] *Ibid.*, **81**, 1279 (1902).
[3] *Z. physik. Chem.*, **105**, 356 (1923).
[4] *Ber.*, **56**, 696 (1923).
[5] *Z. physik. Chem.*, **85**, 351 (1913).

"The osram lamps (4 × 16 candle power) require per second 4 × 16 watt seconds; of this, according to Leimbach (*Z. wiss. Phot.*, **8**, 365 (1910)) about 20 per cent is lost in the lead wires; the remainder is radiated in such a way that there is sent out horizontally twice as much as there would be if it was radiated equally in all directions from the bulb. The surface of our reaction vessel was 3 × 25 cm.², the distance from the lamp 80 cm. Of the total radiation, according to Wien's law, assuming a black body radiation of a temperature $T = 2000°$, about 0.04 per cent lies between 3000 Å. and 5000 Å., the active region according to Bunsen and Roscoe. Finally, in chlorine at one half atmosphere pressure about 5 per cent of the light is absorbed.

Hence the energy absorbed per second is

$$4 \times 16 \times 0.8 \times 2 \times \frac{3 \times 25}{78{,}000} \times 0.0004 \times 0.02 = a \text{ watt secs.}$$

or

$$a \times 0.24 \times 42 \times 10^6 = 19.9 \text{ Ergs.}$$

or, for $\lambda = 4000$ Å.,

$$\frac{19.9}{5 \times 10^{-12}} = 4 \times 10^{12} h\nu.$$

In the experiment with the most reactive mixture, 50×10^{-5} mols, or 3.5×10^{20} molecules of chlorine disappeared in one minute, that is, 6×10^{18} per second. The ratio of molecules to quanta is therefore

$$\frac{6 \times 10^{18}}{4 \times 10^{12}} \quad \text{or} \quad 1.5 \times 10^6 \text{ molecules}/h\nu."$$

It is very evident that when all the uncertainties attaching to the calculation are granted, a very considerable number of molecules of chlorine react for every quantum absorbed.

The work of Baly and Barker, already cited, indicates that the deviations from Einstein's law become more pronounced the greater the intensity of illumination, since they found that the maximum reaction velocity increased more rapidly than the intensity of illumination.

The disproportionality between chemical energy and light energy absorbed is confirmed by investigations of Taylor [1] on the interaction of hydrogen and chlorine under the influence of α-particles, and by investigations of LeBlanc and Vollmer [2] on the same reaction under the influence of Röntgen rays. In each of these cases, chlorine to the extent of 10^4 molecules or more is brought into combination by every pair of ions produced in the reaction system by either type of radiation.

Theories of Mechanism: Any satisfactory theory of the mechanism of the hydrogen-chlorine combination must supply an explanation for a variety of phenomena. Of these, the principal are the induction period of Weigert and Kellermann, the inhibitory influence of oxygen, the necessity for water vapor in illumination by visible light, the sensitivity to ultraviolet light in the absence of water vapor, the abnormal ratio of reactant molecules to absorbed energy. The order of the reaction as to chlorine is important, but, as already emphasized,

[1] *J. Am. Chem. Soc.*, **37**, 24 (1915); **38**, 280 (1916).

[2] *Z. Elektrochem.*, **20**, 494 (1914).

the experimental evidence on this point is not unequivocal. The attempts at a satisfactory theory of mechanism are legion. Only the more recent can be considered.

As the outcome of the Bodenstein-Dux investigation, Bodenstein suggested a reaction mechanism involving a photoelectric effect on the chlorine as a primary process. The electron thereby expelled became the catalyst in a series of processes which may be indicated in the equations

$$(1)\quad Cl_2 + \text{Light energy} = Cl_2^+ + \Theta,$$
$$(2)\quad Cl_2 + \Theta = Cl_2^-,$$
$$(3)\quad Cl_2^- + H_2 = 2HCl + \Theta.$$

A succession of reactions (2) and (3) involving alternate capture and release by reaction of an electron would have accounted for the high yield per unit of absorbed energy. Bodenstein also showed that it was in accord with his kinetic equation. Failure to detect ionization in illuminated chlorine [1] led Bodenstein, in spite of the evidence already cited concerning the action of α-particles and Röntgen rays, to adopt a reaction mechanism based upon the transfer of energy from energy-rich hydrogen chloride molecules to either chlorine or oxygen molecules, but not to hydrogen or nitrogen molecules. Bodenstein saw in the ultraviolet absorption spectra of these gases justification for this view. His new formulation [2] of the reaction mechanism is embodied in the following set of equations:

$$Cl_2 + \text{Light} + H_2 = 2HCl(b).$$

The (b) indicates that the molecule is possessed of an abnormally high energy content. The loss of this energy is assumed to occur as follows:

$HCl(b) = HCl$	(Constant $= k_3$),
$HCl(b) + O_2 = HCl + O_2(b)$	(Constant $= k_4$),
$O_2(b) = O_2$,	
$HCl(b) + Cl_2 = HCl + Cl_2(b)$	(Constant $= k_5$),
$Cl_2(b) = Cl_2$	(Constant $= k_7$),
$Cl_2(b) + H_2 = 2HCl(b)$	(Constant $= k_8$).

The $2HCl(b)$ can then repeat one or other of the preceding changes. The kinetic interpretation of these equations leads to the following set of reaction velocity equations:

$$+\frac{d[2HCl(b)]}{dt} + = k_2 I_0[Cl_2] + k_8[Cl_2(b)][H_2],$$

$$-\frac{d[HCl(b)]}{dt} = k_3[2HCl(b)] + k_4[HCl(b)][O_2] + k_5[HCl(b)][Cl_2],$$

$$+\frac{d[Cl_2(b)]}{dt} = k_5[HCl(b)][Cl_2],$$

$$-\frac{d[Cl_2(b)]}{dt} = k_7[Cl_2(b)] + k_8[Cl_2(b)][H_2].$$

[1] Thomson, *Proc. Camb. Phil. Soc.*, **11**, 901 (1901). LeBlanc and Vollmer, *Z. Elektrochem.* **20**, 494 (1914). Kummell, *Z. Elektrochem.*, **17**, 490 (1911).

[2] *Z. Elektrochem.*, **22**, 58 (1916).

From these equations the measured reaction velocity equation may be deduced if k_8 be extremely large—which is suggested by the small influence of hydrogen—and yields

$$-\frac{d[H_2]}{dt} = k_2 \frac{k_5 I_0 [Cl_2]^2}{k_3 + k_4[O_2]},$$

which is in agreement with the experimental results of Bodenstein and Dux provided k_3 is small compared with $k_4[O_2]$. The presence of k_3, the constant for energy loss from activated chlorine, prevents the equation for the velocity from becoming infinite at zero oxygen concentration. We shall see in later sections that there is a definite trend of opinion recently towards some type of energy transfer of the type herein assumed. This represents an early effort to link up such a mechanism with the kinetic studies.

Chapman and Whiston assume that the radiation absorbed by chlorine can be lost by impact with oxygen molecules; but, when the pressure of hydrogen exceeds 15 cm. and possibly at lower pressures, almost all the active molecules of chlorine—the concentration of which is dependent on the oxygen concentration—combine with hydrogen. They derive an equation

$$+\frac{d[2HCl]}{dt} = k \frac{I_0 [Cl_2]}{[O_2] + k_5[H_2]},$$

which is in agreement with their experimental measurements, since k_5 is of small magnitude, being an expression of Chapman and Underhill's observation that hydrogen is a weak inhibitor. This equation offers no solution, however, for the abnormal photochemical yield of the process.

Concerning the theory of the combination, D. L. and M. G. J. Chapman[1] write:

"It has hitherto been assumed that when light is absorbed by chlorine, unstable active chlorine molecules are formed, which by collision with oxygen molecules can lose their activating energy. Oxygen was, in fact, supposed to play the rôle of a deactivating catalyst. For the arguments, based on quantitative measurements and on analogy, in support of this view, previous papers must be consulted. It would, however, now appear to be probable that active chlorine is not deactivated by oxygen alone, but by the joint agency of oxygen and hydrogen. It seems to us that the simplest way of explaining this fact is on the supposition that the active energy is shared between the chlorine and oxygen, and the hydrogen can rapidly remove it from the oxygen. If we represent an active chlorine molecule by the symbol $Cl_2\epsilon$, in which ϵ is the active energy combined with the molecule of chlorine, then in a mixture of chlorine and oxygen the reversible change given by the equation

$$Cl_2\epsilon + O_2 \rightleftarrows O_2\epsilon + Cl_2$$

would take place, and, in the steady state, the proportion of active chlorine to active oxygen would be determined by the mass equation

$$k_2[Cl_2\epsilon][O_2] = k_3[O_2\epsilon][Cl_2].$$

We shall suppose that equilibrium is very rapidly established, that is, that the constants k_2 and k_3 are very large.

"Now, when a gaseous system, in which only an infinitely small amount of chemical change can take place, is absorbing light, the efficient energy absorbed by the molecules is

[1] *J. Chem. Soc.*, **123**, 3079 (1923).

degraded to heat with comparative rapidity. The process of degradation is sometimes accompanied by the phenomena of resonance and fluorescence, which admit of its being investigated; but, as yet, very little is known about the laws which control the change. In the present case, we shall assume that the rate of degradation per unit volume is proportional to the concentration of the active chlorine, and is given by $k_4[Cl_2\epsilon]$, in which k_4 is a constant.

"The usual assumption that the rate of formation of active chlorine is proportional to the rate of absorption of light energy will also be made. It will now be seen that the rate of increase of concentration of active chlorine is given by the equation

$$d[Cl_2\epsilon]/dt = k_1 I[Cl_2] - k_2[Cl_2\epsilon][O_2] + k_3[Cl_2][O_2\epsilon] - k_4[Cl_2\epsilon], \quad \text{(i)}$$

in which I is the intensity of illumination, and k_1 a constant. In the steady state, $d[Cl_2\epsilon]/dt$ is, of course, zero.

"We have now to account for the removal of activating energy from molecules of oxygen by means of hydrogen. The simplest hypothesis is that the active oxygen combines with hydrogen to produce water, the active energy being simultaneously degraded. If the rate of formation of water is given by the normal mass equation, the rate of disappearance of active oxygen attributable to this cause would be given by the expression $k_5[O_2\epsilon][H_2]^2$, in which k_5 is a constant, and the total rate of increase of concentration of active oxygen would clearly be given by the equation

$$d[O_2\epsilon]/dt = k_2[Cl_2\epsilon][O_2] - k_3[Cl_2][O_2\epsilon] - k_5[O_2\epsilon][H_2]^2, \quad \text{(ii)}$$

in which again $d[O_2\epsilon]/dt$ will become zero when the steady state is reached.

"Putting $d[Cl_2\epsilon]/dt = 0$ and $d[O_2\epsilon]/dt = 0$ in equations (i) and (ii) and solving for $[Cl_2\epsilon]$, we obtain

$$[Cl_2\epsilon] = \frac{k_1 I[Cl_2](k_3[Cl_2] + k_5[H_2]^2)}{k_2 k_5[H_2]^2[O_2] + k_4(k_3[Cl_2] + k_5[H_2]^2)}.$$

Remembering that by hypothesis k_2 and k_3 are large in comparison with k_4 and k_5, we see that

$$[Cl_2\epsilon] = \frac{k_1 k_3 I[Cl_2]^2}{k_2 k_5[H_2]^2[O_2] + k_4 k_3[Cl_2]},$$

whence

$$\frac{d[HCl]}{dt} = k_6[H_2][Cl_2\epsilon] = \frac{k_1 k_3 k_6 I[Cl_2]^2[H_2]}{k_2 k_5[H_2]^2[O_2] + k_4 k_3[Cl_2]} \quad \text{(iii)}$$

in good agreement with the equation deduced from the experimental results.

"It will, no doubt, have been observed that this hypothesis (as well as the older one) implies that the degradation of energy which occurs when hydrogen combines with active chlorine is negligible."

The abnormal yield of the hydrogen-chlorine reaction led Nernst to propose [1] a mechanism in which the primary photochemical process was assumed to be a splitting of a chlorine molecule into atoms. This primary process was then assumed to be succeeded by a chain of reactions resulting in the abnormal yield. In agreement with the observations of Stern and Vollmer already discussed we may write the primary process as occurring through the energy-rich chlorine molecule $[Cl_2]_b$, thus:

$$Cl_2 + h\nu = [Cl_2]_b \rightarrow 2Cl.$$

[1] *Z. Elektrochem.*, **24**, 335 (1918).

The chain reactions which succeed this elementary process are, according to Nernst,

$$Cl + H_2 = HCl + H,$$
$$H + Cl_2 = HCl + Cl.$$

Nernst showed, by thermodynamic reasoning analogous to that given in the cases of hydrogen bromide and iodide (p. 1215), that both of these reactions are accompanied by free energy decrease and therefore can occur spontaneously. They therefore give rise to a chain of reactions resulting in hydrogen chloride formation, which sequence is only stopped by removal of the active atoms by collision with each other or by reaction with oxygen or other inhibitor.

This reasoning suggested that, were a suitable acceptor for chlorine atoms present, no chain reactions would ensue and the law of the photochemical equivalent would be fulfilled. This was realized in Nernst's laboratory, the action of chlorine on trichlorbrommethane being shown by Noddack [1] to be photosensitive and obeying the equivalent law. The action of bromine on hexahydrobenzene was, in the course of the same investigations, shown by Pusch [2] to be in agreement with the Einstein law.

Coehn's interpretation [3] of the chain reactions is a modification of Nernst's, to take account of the different sensitivities of dried gases to visible and ultraviolet light, as evidenced by the work of Coehn and Jung. For the two wavelength regions, two mechanisms are assumed:

I. *Moist; visible light.*

$$\left.\begin{aligned} Cl_2 + h\nu \text{ (small)} &= [Cl_2]_b \\ [Cl_2]_b + Cl_2 &= Cl_2 + 2Cl \end{aligned}\right\} \text{Primary process.}$$

$$\left.\begin{aligned} Cl + H_2O &= HCl + OH \\ OH + H_2 &= H_2O + H \\ H + Cl_2 &= HCl + Cl \end{aligned}\right\} \text{Chain reactions.}$$

II. *Dry; ultraviolet light.*

$$\left.\begin{aligned} Cl_2 + h\nu \text{ (large)} &= [Cl_2]_b' \\ [Cl_2]_b' + Cl_2 &= Cl_2 + 2Cl \\ [Cl_2]_b' + H_2 &= Cl_2 + 2H \\ H + Cl_2 &= HCl + Cl \\ 2Cl &= Cl_2 \end{aligned}\right\} \text{No chain.}$$

No chain reactions are assumed in the ultraviolet reaction with dry gases. The system should therefore obey the law of the equivalent. Experimental test is promised by Coehn.

Weigert [4] objects to Coehn's chain mechanism for the moist gases, since it involves water molecules in the chain mechanism and therefore in the yield

[1] *Z. Elektrochem.*, **27**, 359 (1921).
[2] *Z. Elektrochem.*, **24**, 337 (1918).
[3] *Ber.*, **56**, 696 (1923).
[4] *Z. physik. Chem.*, **106**, 426 (1923).

of the process and the reaction velocity. The data of Bodenstein and Dux as to the absence of effect of water vapor between wide limits contradicts this. Weigert therefore assumes water to be a component of the primary photochemical system, which must be a mixture of the gases in agreement with the observations of Bodenstein and Taylor and of Vollmer (p. 1220). Weigert, therefore, assumes, in agreement with an earlier proposal of Mellor,[1] that, for the primary process, chlorine, hydrogen and water vapor must be present, forming a light sensitive system. The primary process is then, according to Weigert, an inner photoelectric effect between a hydrogen and a chlorine molecule leading to the formation of gas ions, thus:

$$H_2 + h\nu + Cl_2 = H_2^+ + Cl_2^-,$$

which is then followed by

$$H_2^+ + Cl_2^- = HCl + H + Cl,$$

$$\left.\begin{array}{r} H + Cl = HCl \\ 2H = H_2; \quad 2Cl = Cl_2 \end{array}\right\} \text{ or the Nernst chain mechanism.}$$

Weigert assumes that the water vapor intensifies this effect by forming adsorption complexes with the other two gases bringing the hydrogen and chlorine molecules into closer proximity With respect to the inner photoelectric effect it is apparent that the light must activate the hydrogen in some way. Weigert points out that, although hydrogen of itself absorbs only in the extreme ultraviolet, a molecule in the immediate neighborhood of a chlorine molecule with a large electron affinity may be made to yield an electron by a lesser quantum, whose magnitude is smaller the nearer the two molecules are.[2]

Baly and Barker's explanation [3] of the abnormal yield is practically identical with that of Bodenstein already cited. They assume, however, transference of energy from energy-rich hydrogen chloride molecules to hydrogen as well as to chlorine. This is not in accord with the kinetic studies which show that the reaction rate is independent of the hydrogen concentration over considerable ranges.

Further data relative to the equivalence law in respect to exothermic reactions may be obtained from the recent work of Bowen.[4] He has shown, by preliminary measurements, that the photochemical decomposition of carbon tetrachloride solutions of chlorine peroxide and of chlorine monoxide under the influence of violet light appear to agree with the equivalence law. Solutions of nitrogen trichloride in similar circumstances give less certain results not far removed from the requirements of the law.

In continuation of this work, Bowen shows that in the decomposition of gaseous chlorine monoxide the ratio is two molecules decomposed per quantum of light absorbed of a mean wave-length of 4600 Å., in which the quantum is

[1] *J. Chem. Soc.*, **81**, 1293 (1902).
[2] Cf. also Ludlam, *Phil. Mag.*, **23**, 757 (1912).
[3] *J. Chem. Soc.*, **119**, 653 (1921).
[4] *J. Chem. Soc.*, **123**, 1199, 2328 (1923).

therefore $h\nu = 4.28 \times 10^{-12}$ erg. The rate was strictly proportional to the light intensity when this was varied in the ratio 1 : 4. Chlorine as impurity is apparently without effect on the rate of reaction.

Two mechanisms appear to be possible:

(*a*) $$Cl_2O + h\nu = \text{"Active" } Cl_2O \rightarrow Cl_2 + O$$

and

$$Cl_2O + O = Cl_2 + O_2 + 91{,}000 \text{ cals.}$$

or

(*b*) $$Cl_2O + h\nu = \text{"Active" } Cl_2O,$$

$$\text{"Active" } Cl_2O + Cl_2O = 2Cl_2 + O_2 + 95{,}000 \text{ cals.}$$

Both possibilities satisfy the condition that the spontaneous reactions shall be exothermic. Bowen further observes that it should be noted that the very large heat evolutions in either case do not lead to further decomposition as would be expected if the views of Baly that this energy would be liberated at infra-red frequencies capable of reabsorption were universally true.

Experimental confirmation of the Nernst chain mechanism was sought by Bodenstein [1] in some recent work relative to the permeability of iron to hydrogen. The hydrogen diffuses through the metal in the atomic condition. Bodenstein attempted to initiate the hydrogen-chlorine reaction by trying to release hydrogen atoms from the iron into the gaseous system. The experiments gave negative results; this should have been expected, since it is generally accepted, as a result of the experimental work of Langmuir, that hydrogen never leaves a metal surface in the atomic condition. Definite proof that one step in the Nernst chain mechanism actually can occur has been recently obtained by Marshall and Taylor.[2] They have shown that hydrogen atoms, produced by R. W. Wood's method,[3] the passage of a high tension powerful discharge (25,000 volts, 0.12 amp.) through hydrogen at low partial pressures, when led into unilluminated chlorine, give measurable quantities of hydrogen chloride. Experiments are in progress to ascertain whether more hydrogen chloride is produced than can be accounted for by the hydrogen atoms introduced. If this were so, the remaining step in the Nernst mechanism would be experimentally established.

Satisfactory though a chain mechanism of the Nernst type appears to be to account for the abnormal deviation from the law of the equivalent in the case of the hydrogen-chlorine reaction, it must be observed that such a chain mechanism is impossible in a number of reactions in which deviations from the law of the equivalent are known. The chlorination of methane and the union of carbon monoxide and chlorine [4] are photosensitive reactions giving

[1] *Z. Elektrochem.*, **28**, 517 (1922).

[2] *Nature*, **112**, 937 (1923).

[3] *Proc. Roy. Soc.*, **102A**, 1 (1922).

[4] *Z. physik. Chem.*, **42**, 257 (1903); *J. Chem. Soc.*, **99**, 1726 (1911); *Z. physik. Chem.*, **85**, 373 (1913).

abnormally large yields. A slight consideration will show that a chain of the hydrogen-chlorine type cannot be set up for these cases, since both the methane and the carbon monoxide are molecules incapable of the atomic existence presumed in the hydrogen-chlorine chain. Nernst and Noddack,[1] therefore, suggest that it is probably better to assign the abnormal reactivity to transference of energy from the energy-rich chlorinated product to further chlorine molecules. It will be noted that this is a return to the second concept of Bodenstein (p. 1224), put forward in 1916. This concept of energy transfer by collision seems to be the only possible explanation at present for abnormal yields in certain reactions subsequently to be discussed and in certain cases of optical sensitization treated in later sections.

The Light Sensitivity of Silver Compounds: The reactions already treated have been confined to gaseous and liquid systems. The energetics of photochange has been investigated thoroughly in two solid systems. Weigert[2] has studied the photo-chemistry of silver chloride in a printing out paper; Eggert and Noddack[3] have studied specially prepared silver bromide-gelatine emulsions on plates.

Pure silver halides show little if any sensitivity to light. The blackening action of visible light is the more pronounced the more the adsorbed silver salt.[4] Adsorption extends the spectral sensitivity of the photo-halide. Photographic experience has shown that the gelatin of the emulsion and the colloidal silver produced during the "ripening" of the emulsion also increase the photosensitivity of the silver halide.[5]

Weigert's measurements show that, with a silver chloride gelatine emulsion containing a known excess of soluble silver salts, the silver produced on exposure to light comes practically exclusively from the soluble silver salts. With increasing time of illumination, the curve for increase of silver produced is a typical S-shaped curve of the autocatalytic reaction type or what is perhaps better characterized as the type shown by reaction at the boundary of phases (see Chapter XV, p. 981). The silver produced increases the spectral sensitivity of the emulsion. With monochromatic blue light, Weigert established that the photochemical yield was considerably less than the absorbed light. Assuming, however, that the metallic silver was the real photosensitive constituent of the system, Weigert showed that the ratio of reaction produced to light absorbed by metallic silver was much more nearly unity, 1 molecule per $h\nu$, and approached unity for low concentrations of metallic silver in the emulsion. Weigert therefore sees in the printing-out-paper process a complete confirmation of the Einstein law of the equivalent.

Eggert and Noddack used for their investigations silver bromide-gelatine emulsions containing respectively 0.90 mg. and 0.42 mg. silver per square cm.

[1] *Sitz.-ber. preuss. Akad.*, 112 (1923).
[2] *Sitz.-ber. preuss. Akad.*, 641 (1921).
[3] *Ibid.*, 631 (1921); 116 (1923).
[4] Frankenburger, *Z. physik. Chem.*, **105**, 255 (1923).
[5] For comprehensive discussion see Renwick, Hurter Memorial Lecture, *J. Soc. Chem. Ind.*, **39**, 156 T (1920).

They measured the reflected, absorbed and transmitted light, and determined the silver produced by fixing the plates with sodium thiosulphate, estimating the residual silver in the gelatine. They conclude, from the experimental measurements, that, with weak illumination, the law of the equivalent is fulfilled for both types of plate at wave-lengths of 4360, 4050 and 3650 Å. With increasing illumination the yield falls, which they attribute to recombination of the silver and bromine atoms produced in the light, when these are produced in that portion of a grain around which the surrounding gelatine, which normally acts as an acceptor for the bromine, is already brominated. When other acceptors for bromine are present in the reaction system, e.g., silver nitrate, alkalis or water, the proportionality between silver produced and light energy absorbed obtains at much higher proportions of absorbed light. This is evident from the accompanying table for dry and wet plates.

TABLE VI

PHOTOCHEMICAL EQUIVALENT LAW FOR SILVER BROMIDE EMULSIONS

No. of quanta absorbed	Molecules per $h\nu$ Dry plates	Molecules per $h\nu$ Wet plates
14×10^{16}	0.50	0.89
50×10^{16}	0.22	0.43

Weigert objects [1] to some of the assumptions involved in the calculations of Eggert and Noddack and claims that the photochemical yield is considerably less than that calculated by the authors from their results. It is evident that only under ideal circumstances is the Einstein law obeyed exactly for such solid systems.

PHOTO-SENSITIZATION

It was noted in an earlier section that it is not necessary that the reacting species absorb the activating radiation in a photosensitive system. Photoreactions may result from the absorption of light by one of the non-reactants of the system. This was shown by Vogel [2] in 1873 in respect to the silver halides in photographic processes. The spectral region to which the photohalides are sensitive can be extended by bathing the emulsions in suitable dyestuffs. This discovery is the basis of the production of panchromatic photographic plates, and is a most important example of photo-sensitization. The role of chlorophyll in the synthesis of plants seems also in part to be that of an optical sensitizer, making the reaction system, carbon dioxide and water, sensitive to the visible rays of sunlight. A variety of photo-sensitizations of bacteria by fluorescent substances rendering the bacteria sensitive to illumination have an importance in the study of the biology of light processes.[3]

[1] *Z. Physik*, **18**, 232 (1923).

[2] *Ber.*, **6**, 1305 (1873).

[3] Tappeiner and Jodlbauer, Die sensibilisierende Wirkung fluoreszierender Substanzen, Leipzig, 1907.

Such complex systems are of slight avail when the mechanism of photo-sensitization is under study. Fortunately, Weigert succeeded in showing [1] that the phenomenon is also to be found among gaseous systems. He showed, for example, that phosgene, which is a colorless gas absorbing in the ultra-violet only, can be decomposed photochemically by visible light when chlorine is added to the phosgene. The chlorine absorbs the blue light and this energy is transferred by some mechanism to the phosgene, bringing about its decomposition.

$$COCl_2 = CO + Cl_2.$$

Weigert showed that this photo-sensitization is quite a general phenomenon in that the decomposition of ozone can be made sensitive in the visible region by addition of chlorine or bromine, the combination of hydrogen and oxygen and of sulphur dioxide and oxygen can be sensitized to visible light by chlorine.

Bromine sensitizes the conversion of maleic to fumaric acid by visible light as was shown by Bruner.[2] Uranium salts and ferric salts also act as sensitizers, as Neuberg revealed,[3] in the oxidation of benzoic to salicylic acid and in the decomposition of hydrogen peroxide. Pinnow [4] studied the sensitization of the oxidation of hydriodic acid by oxygen in the visible region, quinine and acridine acting as sensitizing agents. Many reaction types in various media are therefore subject to photo-sensitization. We shall study the mechanism more closely in the case of certain gas reactions.

The Decomposition of Ozone: In the dark, when catalytic effects are excluded, ozone is stable. When illuminated with the ultraviolet light which ozone absorbs, decomposition occurs, the rate of pressure increase resulting from the reaction

$$2O_3 = 3O_2,$$

being that corresponding to a first order reaction when the absorption is complete. For weak absorption, this would mean a velocity proportional to the square of the ozone concentration.[5] From the data of Weigert, it has been calculated by Bodenstein [6] that, from 100–1000 molecules of gas are decomposed per light quantum, with indications of an inhibitory power of oxygen on the reaction.

It was thought that, in visible light, ozone was stable; recent investigations by Griffith and Shutt,[7] initiated as a result of calculations made by Lewis [8] in 1918 on the basis of the radiation theory of chemical action, have served to show that ozone may be decomposed by visible light of wave-length longer

[1] *Ann. Physik.*, (4) **24**, 55, 243 (1907).
[2] *Sitz.-ber. Krak. Akad.*, 192 (1910).
[3] *Biochem. Z.*, **27**, 271 (1910).
[4] *Ber.*, **34**, 2828 (1901).
[5] Regener, *Ann. Physik.*, **20**, 1033 (1906); Weigert, *Z. physik. Chem.*, **80**, 78 (1912).
[6] *Z. physik. Chem.*, **85**, 357 (1913).
[7] *J. Chem. Soc.*, **119**, 1948 (1921).
[8] *Trans. Farad. Soc.*, **17**, 579 (1922).

than 6700 Å. and, therefore, in the red region of the visible spectrum. This prediction by Lewis and subsequent verification by Griffith and Shutt constitutes one of the positive achievements of the radiation theory.

As regards the sensitization to visible light by the addition of chlorine, Weigert showed,[1] in an intensive investigation, the far-reaching proportionality between light absorbed and ozone decomposition, independent of the ozone concentration within wide limits. An estimate of the photochemical yield by Bodenstein [2] showed the ratio of absorbing to reacting molecules to be of the order of unity.

The sensitized reaction has been recently studied by Bonhoeffer [3] from the standpoint of the quantum relationship and the law of the photochemical equivalent, using approximately monochromatic illumination (λ = 4360 Å. and a group at 4060 Å.), measuring, with every refinement, the energy involved and chemical reaction produced. Chlorine and bromine were used as sensitizers. It was shown that, with chlorine, the rate of reaction was strictly proportional to the absorbed light, independent of the ozone concentration between concentrations of 5 and 0.1 per cent. The velocities with monochromatic radiation were, naturally, considerably less than in Weigert's studies with a whole spectral region. The following table shows in the last column the number of ozone molecules decomposed per quantum of the mean frequency employed. It is evident that the mean value of $\frac{N}{h\nu}$ is about 2.

TABLE VII

DECOMPOSITION OF OZONE IN PRESENCE OF CHLORINE

Initial Ozone Concentration	Chlorine Content of Mixture	Incident Radiation in Lumen-secs.	Absorption $1 - \frac{I}{I_0}$	$h\nu \times 10^{-18}$ Abs.	Molecules Decomposed $= N \times 10^{-18}$	$\frac{N}{h\nu}$
0.5	40	0.37	0.50	2.07	4.69	2.33
0.5	75	0.40	0.72	3.25	6.42	1.99
0.7	50	0.43	0.58	2.83	5.78	2.03
1	50	0.43	0.58	2.83	5.40	1.84
1	50	0.43	0.58	2.83	6.30	2.25
3	40	0.40	0.50	2.19	4.24	1.94
5	45	0.42	0.54	2.51	4.47	1.79

With bromine vapor as sensitizer, the reaction was more difficult to study. The dark reaction amounted to 10–20 per cent of the sensitized reaction. The remarkable result of the quantitative investigation can be gathered from the observation that in four different experiments the values for $\frac{N}{h\nu}$ were 34.5, 28.2,

[1] *Z. Elektrochem.*, **14**, 591 (1908).
[2] *Z. Elektrochem.*, **19**, 840 (1913).
[3] *Z. Physik*, **13**, 94 (1923).

33.2 and 28.2 or, in the mean, 31. No simple ratio exists, therefore, in the bromine sensitized reaction, between absorbing and reacting molecules.

In his discussion of the experimental results Bonhoeffer stresses the remarkable nature of the observation that the reaction velocity is independent of ozone concentration within the limits 5–0.1 per cent. This points to a remarkable "life" of the activated chlorine molecule, since, in the more dilute ozone mixture, such a molecule must meet 1000 molecules of chlorine and oxygen before it reaches an ozone molecule. This would cast doubts on the mechanism postulated, in the hydrogen-chlorine combination, for the inhibitory power of oxygen. From kinetic data, Bonhoeffer calculates a minimum life of 1.6×10^{-7} sec. That two molecules of ozone are decomposed is in agreement with data on the photo-sensitivity of ozone itself.

That, in the case of bromine sensitization, more than thirty ozone molecules decompose for every activated bromine molecule compels us, in the view of Nernst and Noddack,[1] to assume that energy must be transferred from activated ozone molecules to inactivated, or that the energy of the reaction products may be so transferred.

His own earlier data and the confirmatory data of Bonhoeffer have led Weigert to a detailed consideration[2] of the theory of the transformation of radiation. Weigert sees in the ozone-chlorine sensitized reaction the simplest case of chlorine photo-reactions and he would therefore expect to draw from the reaction the simplest conclusions as to mechanism. He points to the importance of the fact that the velocity of reaction is independent of the ozone concentration at a certain, but small, ozone concentration, as showing that, at and above this concentration, *all* or practically all the radiant energy absorbed by the chlorine is converted into chemical energy. Similar observations have been made by Grüss[3] for two sensitized reactions involving trichlor-brom-methane,

$$2CCl_3Br + Cl_2 = 2CCl_4 + Br_2,$$

$$2CCl_3Br + O_2 = 2COCl_2 + Br_2 + Cl_2.$$

With chlorine, free from ozone, but containing moisture or other impurities in small quantities, light may be absorbed and converted completely into heat energy, as shown by chlorine in the **Budde effect,**[4] the expansion due to temperature rise when moist chlorine is illuminated.

Weigert sees a complete analogy to these two modes of transformation of light energy in experiments with mercury vapor. In pure mercury vapor at low pressures, Wood[5] showed that the resonance line, 2536 Å., can readily be stimulated by illumination with a mercury vapor lamp. By addition of air or other gases, this resonance radiation can be suppressed entirely. In

[1] *Sitz.-ber. preuss. Akad.*, 113 (1923).
[2] *Z. physik. Chem.*, **106**, 403 (1923).
[3] *Z. Elektrochem.*, **29**, 144 (1923).
[4] *Pogg. Ann.*, **144**, 213 (1871); *Ergbd.*, **6**, 477 (1873).
[5] *Phil. Mag.*, **18**, 187 (1909); *Physik. Z.*, **10**, 425 (1909).

this event, Wood says that a true absorption occurs, the light energy introduced being converted into heat. Now, it has recently been shown by Cario and Franck [1] that the light energy can be transformed into chemical energy if the gas added to the mercury vapor is hydrogen. These authors showed that an illuminated system of mercury vapor and hydrogen decreased in pressure, owing to the production of hydrogen atoms which "cleaned up" [2] on the walls of the containing vessel or could reduce copper oxide at ordinary temperatures. According to Cario and Franck, there exists also, in this case, a limiting hydrogen pressure above which all the absorbed light energy is converted into chemical energy.

The limiting pressures of the reacting species, of ozone at 0.5 mm. or lower and of hydrogen at 10 mm. Hg pressure, and the pressures of the sensitizing agents (chlorine 0.5 atm., and mercury 0.009 mm.) are quite different. The ratio of reacting to sensitizing molecules is also different; for the ozone-chlorine reaction $\frac{n_r}{n_s} = 1.3 \times 10^{-3}$ and for the mercury-hydrogen, 1.1×10^{3}. If, however, Weigert points out, one calculates the number of reacting molecules which are to be found in photochemically comparable volumes of a cylindrical vessel, corresponding to the thickness through which the absorbed radiation is reduced to the same extent, practically identical numbers are obtained in the two cases. This occurs by reason of the strong absorption of mercury vapor and the small absorption of chlorine. Weigert therefore thinks it probable that the processes are quite analogous to one another.

The weakness of Bonhoeffer's concept of a long-lived chlorine molecule, unable to lose its energy to oxygen or other chlorines but only to ozone when chemical reaction ensues, is evident when the mercury cases are considered. Under given conditions, all three types of phenomena, resonance radiation, heat and chemical reaction can result from one and the same primary photoprocess, the absorption of light from the mercury vapor lamp. Weigert, therefore, assumes that in the ozone-chlorine reaction the same process occurs as in the mercury reactions. The radiation absorbed by the chlorine is first emitted as isochromatic resonance radiation in the normal way and this absorption and emission process is repeated continuously by the chlorine until, finally, absorption in a binary system (involving ozone simultaneously; see page 1228) leads to an inner photoelectric effect and to chemical change or to a change in translatory energy of the particles.

The resonance radiation of the mercury can be perceived because of the extraordinarily strong absorption of the exciting light; with chlorine it is imperceptible because the absorption is a hundred million times smaller. On the other hand, there is indirect evidence of its occurrence. For, the Budde effect only occurs with moist chlorine or chlorine containing small impurities. With pure dry chlorine, no Budde effect is observed although absorption

[1] *Z. Physik*, **12**, 162 (1922).

[2] Langmuir, *J. Am. Chem. Soc.*, **36**, 1710 (1914); **37**, 417 (1915); **38**, 1145 (1916).

occurs. Weigert assumes that, in this case, the absorbed energy is re-emitted as isochromatic resonance radiation.

This mechanism of Weigert is in agreement with his observation (p. 1219) that perceptible time intervals occur during which the observed chemical change is completed. It does not explain abnormal yields of chemical energy. To explain such, some type of chain mechanism or of energy transference from products to reactants must be assumed.

Catalytic Effects in Ozone Decomposition: Various gases have been found to accelerate ozone decomposition; optical sensitization cannot be the cause of the acceleration observed since the gases do not absorb the wave-lengths employed. Weigert [1] and Weigert and Bohm [2] have studied the decomposition of ozone by ultraviolet light in the presence of hydrogen. Pronounced acceleration is produced. Griffith and Shutt [3] have studied the same system in visible light and Griffith and MacWillie [4] have studied the reaction in the presence of helium, argon, nitrogen, carbon monoxide and carbon dioxide.

Weigert assumes that the decomposition of ozone in the presence of hydrogen is not a photochemical process but a thermal reaction. The heat liberated by the reaction

$$[O_3]_b + H_2 = O_2 + H_2O$$

is supposed to warm the gas in the neighborhood of the absorbing layer to a temperature high enough to enable the bimolecular thermal reaction

$$2O_3 = 3O_2$$

to proceed at an appreciable rate. Griffith and Shutt reject this mechanism for visible light since there is no greater increase in temperature on illumination of gas mixtures containing hydrogen than in those containing ozone and oxygen alone. Griffith and Shutt suggest that the water molecules formed, which for some period after their formation can possess energy, can activate ozone molecules by collision. In the absence of hydrogen the ozone decomposition is much slower and is bimolecular, in agreement with the ultraviolet reaction with weak absorption.

With carbon monoxide present in the ozone mixture, reactions similar to those with hydrogen can occur. With the other gases present, only the ozone decomposition

$$2O_3 = 3O_2$$

occurs, the velocity being greatest with helium admixed, less so in order with argon, nitrogen and carbon dioxide, least of all with oxygen-ozone mixtures alone, comparisons being made at the same ozone concentration. Were the admixed gases acting as diluents to an inhibitory oxygen concentration (see page 1232) the specific order given would not be anticipated—they would all be expected to have a like action. Griffith and MacWillie therefore suggest

[1] *Ber.*, **46**, 815 (1913).
[2] *Z. physik. Chem.*, **90**, 194, 233 (1915).
[3] *J. Chem. Soc.*, **123**, 2752 (1923).
[4] *J. Chem. Soc.*, **123**, 2767 (1923).

that the order of efficiency is an index of the efficiency of the admixed gas in causing de-activation of the ozone molecules by collision.

The Stationary State or Photochemical Equilibrium

Every reversible reaction, in which one or both directions of change are sensitive to light, will produce, with a given intensity of illumination, a definite "equilibrium" or stationary state. This state will be dependent, obviously, on the concentrations of the reacting substances, on the temperature, on the illumination employed both as to intensity and frequency, and on the velocity with which the two reactions occur under such conditions. It follows also, from thermodynamic considerations, that the shift of the normal "dark" equilibrium shall never be in that direction in which a perpetuum mobile is possible;[1] that is, the change in free energy occurring must come from the radiant energy supplied.

The simplest case will be found with a reaction light sensitive in one direction only. Such a case has been well investigated and will now be discussed.

The Polymerization of Anthracene: Solutions of anthracene when exposed to ultraviolet light undergo polymerization of the anthracene to form dianthracene. The reaction

$$2C_{14}H_{10} = C_{28}H_{20}$$

is reversible, the depolymerization, which is not photosensitive (see, however, below, p. 1238), occurring spontaneously in the dark. Upon illumination, therefore, a definite stationary state is finally attained dependent, at a given temperature, on the light intensity. The reaction has been studied in detail by Luther and Weigert.[2] The depolymerization or dark reaction was found to be pseudo-unimolecular at all temperatures, practically complete, and to have a large temperature coefficient (circa 2.8 for 10°). The polymerization or light reaction was of zero order for complete absorption, between zero order and first order for partial absorption. The reaction is, therefore, evidently determined by the amount of light absorbed. As already discussed, the reaction obeys approximately the law of the photochemical equivalent (see page 1211). The temperature coefficient for the light reaction is small and equal to about 1.1 for 10° C. Several solvents were tried, including phenetol, anisole and xylol. The solvent exercises a specific influence upon both the velocities and the equilibrium. It is evident that the reaction occurring at a given temperature can be expressed by an equation of the form

$$\frac{dx}{dt} = k_l I_{abs} - k_d x,$$

where x is the dianthracene formed, I_{abs} the light energy absorbed, k_l and k_d specific constants of the light and dark reactions. At equilibrium, or the stationary state,

$$k_l I_{abs} = k_d x.$$

[1] Bodenstein, *Z. physik. Chem.*, **85**, 382 (1913).

[2] *Z. physik. Chem.*, **51**, 297 (1905); **53**, 385 (1905); **62**, 454 (1908); *Ber.*, **42**, 859 (1909).

This equation summarizes the influence of various factors upon the equilibrium state. It is apparent that x depends on the value of the specific constants k_l and k_d and on the intensity of light absorbed. It will also vary, at constant intensity, with temperature, since, under such conditions,

$$x = I_{abs} \frac{k_l}{k_d}.$$

As already pointed out, k_l and k_d vary differently with temperature, k_l has a temperature-coefficient of 1.1 per 10° and k_d 2.8 per 10° C. The equilibrium concentration at a given intensity will therefore decrease in the ratio $\frac{1.1}{2.8}$ for a 10° rise in temperature. These conclusions were experimentally verified.

H. A. Taylor and Lewis [1] have recently reinvestigated the photo-polymerization process from the standpoint of the radiation theory of chemical reaction. In phenetol solution, two absorption bands are found in the blue violet at 4450 and 4750 Å. In the infra-red region, anthracene in phenetol shows a band at 1.8 μ only. The energy quantity corresponding to $\lambda = 4600$ Å is approximately 61,000 cals. Were this quantity absorbed by two anthracene molecules before polymerization, an absorption band should be observed at 9200 Å. or 0.9 μ. The spectroscopic observation showing this to be absent, the conclusion is reached that the polymerization consists in the activation of a molecule of anthracene by radiant energy of wave-length 4600 Å. and that this molecule then combines with a non-activated molecule to give the polymer.

Since, as shown by Weigert, the concentration of dianthracene in solution in thermal equilibrium increases as the temperature is raised, dianthracene must be produced with absorption of heat. The magnitude of this heat effect is of the order of 20,000 cals. The critical increment of activation of dianthracene to form anthracene should therefore be (see Chapter XIX)

$$\begin{aligned} E_{\text{dianthracene}} &= E_{\text{anthracene}} - 20{,}000, \\ &= 61{,}300 - 20{,}000, \\ &= 41{,}300 \text{ cals.} \end{aligned}$$

This is approximately the energy quantity corresponding to a reaction with a temperature coefficient of the dark reaction, since the temperature coefficient actually measured, 2.8, corresponds to 39,200 cals. Taking the mean value of these two quantities as 40,000 cals., this corresponds to an absorption by dianthracene at 7070 Å. Actual absorption measurements at this wave-length failed to reveal absorption by the methods employed. It was found possible by exposure of the system to radiation of wave-length 7070 Å. to bring about *photo-depolymerization* of dianthracene. The sensitivity to such radiation was, however, small. To this extent, therefore, the statement, made in the beginning of this section, that the depolymerization is not photo-sensitive needs qualification.

[1] *J. Am. Chem. Soc.*, **46**, 1606 (1924).

Stationary State in Gas Reactions: Coehn and his co-workers have investigated a number of cases of photo-equilibria in gaseous systems. The most thoroughly investigated is the photo-equilibrium in the reversible reaction [1]

$$2SO_3 = 2SO_2 + O_2.$$

In this case, in quartz reaction vessels, neither reaction proceeds thermally at the temperatures employed. It was shown that the reaction was truly reversible in that the same stationary state was reached from both sides. The mass action law equation

$$K = \frac{[O_2][SO_2]^2}{[SO_3]^2}$$

was fulfilled in all cases with variable reactant ratios. The extent of displacement of the thermal equilibrium may be judged from the fact that at 45° C., at which temperature sulphur trioxide is practically undecomposed, as much as 35 per cent decomposition occurred under the given experimental conditions. With increasing intensity of illumination the decomposition of the trioxide increased. With constant illumination, between reaction temperatures of 50 and 800° C., the photo-equilibrium is the same, independent of the gas temperature. This indicates that the temperature coefficient of the two photo-processes is the same, since the thermal reaction does not occur under the given conditions.

Coehn and Wassiljewa [2] investigated the equilibrium

$$2HCl \rightleftarrows H_2 + Cl_2$$

in the same apparatus as was used by Coehn and Becker. A stationary state at 0.25 per cent decomposition of hydrogen chloride was obtained. Coehn and Becker [3] found a photo-equilibrium with phosgene at 3.3–4 per cent decomposition. Coehn [4] found a similar equilibrium with water at 0.2 per cent dissociation, all these equilibria being attained under the conditions of the quartz-mercury vapor lamp which gave 35 per cent decomposition of sulphur trioxide. In the water vapor equilibrium the law of mass action does not apply. This might result if one of the reactants was not activated by the incident radiation.

Treatment of photochemical stationary state from the standpoint of the phase rule has been given by Wildermann [5] and by Bancroft.[6] The latter assumes an additional degree of freedom for each kind of light present.

[1] Coehn and Becker, *Z. Elektrochem.*, **13**, 545 (1907); *Z. physik. Chem.*, **70**, 88 (1909).
[2] *Ber.*, **42**, 3813 (1909). See also Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916).
[3] *Ber.*, **43**, 130 (1910).
[4] *Ber.*, **43**, 880 (1910); *Nernst Festschrift*, p. 136, Halle, 1912.
[5] *Z. physik. Chem.*, **42**, 331 (1903).
[6] *J. Phys. Chem.*, **10**, 721 (1906).

The Inhibition of Photochemical Reactions

The classical example of inhibition in a photochemical reaction is the case of the retardation of the hydrogen-chlorine combination by oxygen. The mechanism of this inhibition has already been discussed and so does not need to be repeated here. It is of interest to note that, in several other photohalogenation reactions, a similar influence of oxygen as inhibitor is manifest. Thus, for example, in the formation of phosgene [1] and in the bromination of toluene [2] this inhibitory power is to be noted.

No general formulation of inhibitory action seems to be possible. Widely varying types of inhibition may be met with one and the same reaction. This may be illustrated in the case of decomposition of hydrogen peroxide.

The Decomposition of Hydrogen Peroxide: Early studies of Tian [3] on the kinetics of decomposition indicated that the reaction velocity is unimolecular. Henri and Wurmser showed [4] that the absorption of light is so weak that as many as 100 molecules of the peroxide are decomposed for every quantum of absorbed energy. This conclusion has been completely verified by a careful study of Kornfeld,[5] using monochromatic illumination and exact methods of energy absorption measurements. As with the thermal decomposition of hydrogen peroxide, the photochemical change is very sensitive to added substances, some of which promote decomposition, many of which inhibit decomposition. Henri and Wurmser [6] presented a number of inorganic compounds which inhibit the light reaction and in the following year Mathews and Curtis [7] added a number of organic and inorganic compounds. These latter authors failed to observe any properties possessed in common by the inhibitors. Recent investigations by Anderson and Taylor [8] have tended to elucidate the mechanism of certain inhibitions. The inhibitory effects exhibited by typical organic compounds of known absorption spectra were examined in four definite spectral regions of the ultraviolet. The inhibition by such agents was associated with the absorption capacity of the compounds for the ultraviolet light. A striking correlation between these two factors was obtained in the case of benzene, several esters, acids, amides, ketones and alkaloids. The inhibitors act more efficiently when in the peroxide solution than when in a screening solution of similar thickness and concentration. This is doubtless to be associated with the abnormal photochemical yield per quantum absorbed. These inhibitors apparently act therefore in a twofold capacity. They absorb some of the radiation which might activate hydrogen peroxide molecules. They apparently, also, break whatever chain mechanism may be set up [9] to account

[1] *Z. physik. Chem.*, **42**, 257 (1903); *J. Chem. Soc.*, **99**, 1726 (1911).
[2] *Sitz.-ber. Krak. Akad.*, 576 (1910).
[3] *Compt. rend.*, **151**, 1040 (1910).
[4] *Ibid.*, **156**, 1012 (1913).
[5] *Z. wiss. Phot.*, **21**, 66 (1921).
[6] *Compt. rend.*, **157**, 284 (1913).
[7] *J. Phys. Chem.*, **18**, 521 (1914).
[8] *J. Am. Chem. Soc.*, **45**, 650, 1210 (1923).
[9] See Kornfeld, *loc. cit.*, and Nernst and Noddack, *Sitz.-ber. preuss. Akad.*, 112 (1923).

for the abnormal photochemical yield. Not all inhibitors act in the former capacity. Certain aliphatic alcohols and amines, hydrogen, halogen and hydroxyl ions act as inhibitors although quite diactinic in the ultraviolet.

Certain photo-oxidations, for example, the oxidation of benzaldehyde, are also retarded by traces of added substances. It is of interest to note that several of these oxidations appear to be chain mechanisms in that an abnormal yield per quantum absorbed is obtained. The inhibitor may act by breaking the chain as postulated for negative catalysts in both photochemical and thermal reactions by Christiansen.[1]

Mathews and Dewey [2] and Mathews and Weeks [3] have investigated one such oxidation in detail, that of sodium sulphite. They find both accelerators and retarders of oxidation. Uranium salts are positive catalysts for the photo-reaction, presumably by photo-sensitization. Copper salts, which Titoff [4] showed to be remarkably powerful catalysts for the thermal process, are without action photochemically. Pyridine, benzaldehyde, phenol, hydroquinone, quinine sulphate, ethyl acetate, urea were all retarding agents of varying efficiency. From unpublished experiments by Bäckström, in the writer's laboratory, it is evident that this reaction is also one in which many molecules react for each energy quantum absorbed. Bäckstrom has shown the same to be true, also, for the autoxidation of benzaldelyde.

The Temperature Coefficient of Photochemical Change

The temperature coefficient of most photochemical reactions is small, in contrast to that of most thermal reactions. Plotnikow [5] lists 22 photochemical reactions for which the temperature coefficient

$$r = \frac{k_{t+10}}{k_t}$$

has a maximum value of 1.08. He further lists 19 reactions in which the ratio r varies from 1.17 to 1.50. Plotnikow believes that all photo-reactions can be classified in three groups having temperature coefficients respectively 1.03 ± 0.03, 1.27 ± 0.03 and 1.40 ± 0.03. There seems to be little evidence for this classification and reactions are known whose temperature coefficient lies well outside this range, though Plotnikow [6] is inclined to doubt the accuracy of several of these. It was Goldberg [7] who in 1903 first called attention to this low coefficient. Typical examples are given in the following table.

According to Perrin,[8] so long as the temperature is so low that the isothermal radiation practically does not contain the exciting light, the velocity of a photo-

[1] *J. Phys. Chem.*, **28**, 145 (1924).
[2] *J. Phys. Chem.*, **17**, 211 (1913).
[3] *J. Am. Chem. Soc.*, **39**, 635 (1917).
[4] *Z. physik. Chem.*, **45**, 641 (1903).
[5] *Allgemeine Photochemie*, pp. 62–65, Berlin and Leipzig, 1920.
[6] *Loc. cit.*, p. 68.
[7] *Z. physik. Chem.*, **41**, 1 (1903).
[8] *Trans. Farad. Soc.*, **17**, 560 (1922).

TABLE VIII

TEMPERATURE COEFFICIENTS OF PHOTOCHEMICAL REACTIONS

Reaction	r	Reaction	r	Reaction	r
Photographic plate	1–1.06	$C_{14}H_{10} \rightarrow C_{28}H_{20}$.	1.04	$2HI + O_2$ ..	1.39
$H_2 + Cl_2$.	1–1.04	$2O_3 \xrightarrow{Cl_2} 3O_2$	1.17	$CHI_3 + O_2$	1.42
$H_2 + O_2$..	1.08	$SO_2 + O_2$ . .	1.20	$C_6H_6 + Br$..	1.40

chemical reaction will not depend upon the temperature of the body, but will depend solely upon the intensity of the exciting light. It is obvious, however, that a photochemical reaction may involve two species, one only of which is photosensitive, the other of which may require activation. In such cases higher temperature coefficients would be anticipated. This reason is assigned by Bodenstein [1] for the high temperature coefficient, 1.83, of the bromine-toluene reaction studied by Bruner and Dluska.[2]

Tolman [3] has recently attempted a general theoretical treatment of the problem of temperature coefficient of a photochemical reaction. The earlier paper of two gives a treatment based on classical statistical mechanics and applicable only to unimolecular processes. In the latter, the methods of the quantum theory are used and the application is to uni- and bimolecular processes. In the unimolecular process, the mechanism is regarded as consisting in the absorption of a quantum, $h\nu$, which raises the molecule to such an energy level that reaction can take place. The velocity of such a process will be given by the equation

$$-\frac{dC_A}{dt} = k_\nu a_\nu C_A,$$

where k_ν may be called the specific photochemical reaction rate, the rate at unit concentration of the reactant, A, with unit energy density of frequency ν. Tolman obtains an expression for k_ν in terms of the probability that a molecule in a given quantum state will acquire a quantum of energy and of the probability that such a molecule will then undergo the given unimolecular transformation. His expression when differentiated with respect to temperature gives the equation

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{\epsilon'' - \epsilon'}{kT^2},$$

where ϵ'' is the average energy before activation of the molecules which actually pick up radiant energy and react, ϵ' is the average energy of all the molecules.

For a bimolecular process in which only one reactant, A, of the reactants, $A + B$, is activated by the radiant energy an equation similar in form to the

[1] *Z. physik. Chem.*, **85**, 380 (1913).
[2] *Sitz.-ber. Krak. Akad.*, 691 (1907).
[3] *J. Am. Chem. Soc.*, **42**, 2506 (1920); **45**, 2285 (1923).

preceding is obtained,

$$\frac{\partial lnk_\nu}{\partial T} = \frac{1}{2T} + \frac{e'' - e'}{kT^2},$$

where e'' is the average energy of the pairs of molecules of A and B that actually react and e' is the average energy of any pair of molecules A and B. The term $\frac{1}{2T}$ arises from the assumption that the number of collisions of the molecules of the gas is proportional to the absolute temperature.

Differentiation of either of these equations with respect to the frequency gives the result

$$\frac{\partial}{\partial \nu}\left(\frac{\partial lnk_\nu}{\partial T}\right) = \frac{1}{kT^2}\frac{\delta e''}{\delta \nu},$$

which gives the variation of the temperature coefficient with frequency.

To compare these theoretical equations with experimental results it is obviously necessary to make the following transformations:

$$r = \frac{k_{t+10}}{k_t},$$

$$\frac{\partial lnk_\nu}{\partial T} = \frac{k_{t+10} - k_t}{\frac{10(k_{t+10} + k_t)}{2}} = \frac{r - 1}{5(r + 1)}.$$

Now, since r is approximately unity in a number of cases, it follows that, neglecting the small term arising from increased frequency of collisions,

$$\frac{\partial lnk_\nu}{\partial T} = \frac{e'' - e'}{kT^2} = 0.$$

The average energy of the reacting molecules is practically identical with the average energy of all the molecules. This conclusion merely means that the average molecule has as good a chance of picking up energy and becoming activated as the molecules in some special quantum state far removed in energy content from the average.

If some molecules are in low quantum states, unable to absorb radiant energy of the frequency used, or if the energy level which they attain is not high enough to lead to chemical reaction, then preliminary activation of the molecules may be advantageous. In such case,

$$\frac{\partial lnk_\nu}{\partial T} = \frac{e'' - e'}{kT^2} > 0$$

and therefore

$$r = \frac{k_{t+10}}{k_t} > 1.$$

In the case of second order reactions, in addition to the effect of the term $e'' - e'$ in determining temperature coefficients, it is also necessary to consider, as pointed out above, the effect of temperature in increasing the number of collisions between the reacting molecules. In gaseous systems the number of collisions will be roughly proportional to the square root of the absolute temperature and this will produce a negligible increase in reaction velocity with increasing temperature. In liquid systems the decrease in viscosity with rising temperature may be large enough to produce a measurable effect on reaction velocity. Similar considerations will apply to heterogeneous diffusions where diffusion of the reacting substances to a catalytic surface is necessary for reaction. Since the viscosity of water at room temperature decreases about 20 per cent for a 10° rise, this might account, in some cases, as suggested by Plotnikow, for a value $r = 1.20$. It should be noted, however, that of the 7 reactions which Plotnikow lists as belonging to the group with the value 1.20, 3 are gaseous reactions, so that his explanation can hardly be a general one.

Further evidence as to the tenability of the theory of temperature coefficient presented by Tolman is afforded by a calculation of the magnitude of $e'' - e'$. If we write

$$\frac{\partial ln k_\nu}{\partial T} = \frac{e'' - e'}{kT^2} = \frac{r - 1}{5(r + 1)},$$

and take $r = 1.40$ and $T = 300°$ as typical, we obtain for $e'' - e'$ the value 6000 cal. per mol. This corresponds to a value of 0.26 volt per molecule, which is an entirely reasonable figure for the difference in energy contents between successive quantum levels in a molecule.

For test of Tolman's equation on the variation of temperature coefficient with frequency the data are scanty. Nevertheless, silver citrate paper has the temperature coefficient $r = 1.19$ in the blue and 1.07 in the ultraviolet; the phototropic substance, salicylidene-β-naphthylamine, has the values 1.8 in the green, 1.45 in the blue and 1.39 in the violet; and the reaction between chlorine and hydrogen has the values 1.50 for green light (5500 − 5300 Å.), 1.31 for blue light (4900 − 4700 Å.) and 1.21 for violet light (4000 − 3500 Å.). These results are in complete agreement with the theory. Their reliability is not known.

The Temperature Coefficient of Photochemical Yield: Little is known as yet with regard to the relationship between the number of molecules reacting per quantum of light energy absorbed and the temperature of the reacting system. There are indications, however, that this is a fruitful field for further investigations. Kastle and Beatty [1] showed that hydrogen and bromine, which are not photosensitive at ordinary temperatures, are caused to combine by the light of the sun penetrating glass vessels, if the gases are at 200° C. They state that there are indications that the gas mixture is sensitive at 100° C. Lind [2] has shown that at 250° C. this reactivity is quite marked, but states

[1] *Am. Chem. J.*, **20**, 159 (1898).
[2] *J. Phys. Chem.*, **27**, 55 (1924).

that in none of his experiments did the photo-efficiency seem to exceed the simple relationship of the Einstein equation. At 300° C., Anderson has shown, in the writer's laboratory, that the reaction in the light of a quartz-mercury lamp is some 40 per cent greater than that in the dark under the same conditions. The quantum relationship was not studied. It is very evident, however, that somewhere in the region 0–200° C., the ratio of mols. reacting to quanta absorbed must be worthy of study.

Experimental evidence of such a variation with temperature is now available in one case. Kuhn [3] has shown that the velocity of photochemical decomposition of ammonia with light of wave-length, $\lambda = 2025$ to 2140 Å., increases with the temperature, approximately 50 per cent per 100 degrees rise in temperature. The ratio of quanta required to molecules decomposing changes from 2.5 at 20° C. to $0.3h\nu$ per mol. at 500° C. Hydrogen inhibits the decomposition whilst nitrogen is without effect. Kuhn states that these results suggest the following points with reference to mechanism.

A molecule of ammonia absorbs a quantum $h\nu$ (= 128,000 cals. per gram-mol.) and passes to the active state $[NH_3]$.

$$NH_3 + h\nu = [NH_3].$$

A part of these molecules return to the normal state; the others react. This reaction may be decomposition according to the equation

$$[NH_3] = N + H + H_2 + 5000 \text{ cal.},$$

or according to the equation

$$[NH_3] + NH_3 = N_2 + 3H_2 + 104{,}000 \text{ cals.}$$

Atomic nitrogen and hydrogen can in their turn react with ammonia especially at elevated temperatures,

$$N + NH_3 = N_2 + H_2 + H + 17{,}000 \text{ cal.},$$
$$H + NH_3 = N + 2H_2 - 39{,}000 \text{ cal.}$$

These reactions may explain how the absorption of a single quantum at elevated temperatures may lead to two or more molecules decomposing.

The inhibitory power of hydrogen is to be explained, according to Kuhn, by reaction between activated ammonia and hydrogen molecules exactly as in the Cario-Franck case of hydrogen and mercury (p. 1235).

$$[NH_3] + H_2 = NH_3 + 2H + 44{,}000 \text{ cal.}$$

With nitrogen a similar reaction is impossible,

$$[NH_3] + N_2 = NH_3 + 2N - 12{,}000 \text{ cal.}$$

[3] *Compt. rend.*, **177**, 956 (1923); **178**, 708 (1924).

After-Effects from Photochemical Action

In a number of cases the reactions produced by light persist after illumination has ceased. These after-effects are of a certain interest in connection with the mechanism of the photo-change. Kistiakowski observed a photo-decomposition of hydrogen peroxide [1] when exposed in solution along with ferro- and ferricyanides to visible light. The decomposition is pseudo-unimolecular; it persists, however, when illumination is discontinued, with undiminished velocity. The mechanism in this case is clear. The action is to be attributed to the formation of colloidal particles by the action of light on the ferro- and ferricyanides, which particles act as heterogeneous catalysts for the peroxide decomposition. Ultramicroscopic examination of such solutions confirms the assumption of the presence of colloidal particles.

The Oxidation of Iodoform: In alcohol, the oxidation of iodoform proceeds normally. In other solvents, after-effects are produced, the reaction proceeding after illumination has ceased but with a different velocity, as was demonstrated by Plotnikow.[2] In benzol solution, the light reaction continuously increases in velocity with increase in concentration. This is to be attributed to a combined light and dark reaction; the latter proceeds, according to Plotnikow, with a velocity given by the equation

$$K_d = 962[CHI_3]^{1.28},$$

where K_d is the velocity constant of the dark reaction, $[CH_3I]$ the iodoform concentration. The temperature coefficient of the dark reaction is 2.62 as opposed to the light reaction coefficient of 1.4. The relative magnitudes of light and dark reaction vary tremendously with different solvents as revealed by the following table.

TABLE IX

Iodoform Oxidation in Various Solvents

Solvent	$K \cdot 10^6$ For Light and Dark Reaction	$K_d \cdot 10^6$ For Dark After Effect
C_6H_6	40.1	5.5
$CH_3COOC_2H_5$	9.4	0.9
CCl_4	41.8	2.4
CS_2	22.3	0
C_2H_5OH	2.52	0
CH_3COCH_3	0.65	0

The mechanism of the after-effect is unexplained. The effect of various solvents on the rate and the existence of the after-effect is noteworthy. Plotnikow found, by actual test, that the reaction is practically insensitive to catalytic agents added to the reaction system.

Trautz and Thomas [3] have also shown that the oxidation of sodium sulphide,

[1] *Z. physik. Chem.*, **35**, 431 (1900).
[2] *Z. physik. Chem.*, **76**, 743 (1911).
[3] *Physik. Z.*, **7**, 899 (1906); *Z. Elektrochem.*, **13**, 550 (1907); *Z. wiss. Phot.*, **4**, 352 (1906).

of cuprous chloride in hydrochloric acid solution and of benzaldehyde show after-effects when illumination is discontinued. In these studies it was also shown that light of one wave-length may retard whilst another wave-length accelerates a given reaction. The following table reproduces examples of such behavior.

TABLE X

ACCELERATION AND RETARDATION OF REACTION BY LIGHT

Reaction	Velocity in Dark	Velocity in Red Light	Velocity in Violet Light
$Na_2S + O_2$	239	302 (*A*)	160 (*R*)
$Cu_2Cl_2(NH_3) + O_2$	254	270 (*A*)	190 (*R*)
$Cu_2Cl_2(HCl) + O_2$	211	164 (*R*)	59 (*R*)
Pyrogallol + O_2	70	77 (*A*)	55 (*R*)
Benzaldehyde + O_2	20	15 (*R*)	350 (*A*)
H_2O_2 decomposition	62	57 (*R*)	149 (*A*)

These reactions, as is well known, are very sensitive to traces of impurities. The results given must, therefore, be accepted with caution.

That the benzaldehyde oxidation shows an after-effect when illumination has been discontinued has been confirmed by Bäckström in some unpublished work carried out in the writer's laboratory. The magnitude of the effect is greater when inhibitors are present. Inhibitors suppress the thermal reaction much more, proportionately, than they do the photo-reaction. The possibility that the after-effect is to be associated with the known existence of chain reactions in such oxidation processes is receiving investigation.

The action of light on silver halide emulsions is frequently discussed in connection with photo-after-effects. Actually, however, the subsequent development of a latent image produced on a silver halide grain by exposure to light is quite distinct from the initial photo-change. Recent developments in the investigation of the nature of the light reaction in a silver halide emulsion warrant some consideration of this subject, since points of both theoretical and practical importance are involved.

The Latent Image in Silver Halide Emulsions: The literature concerning the nature of the latent image and the sensitiveness of photographic emulsions is so abundant that it is fortunate that a summary of present and past views is available in a recent issue of the *Transactions of the Faraday Society*, in a general discussion[1] of the physical chemistry of the photographic process. In this volume the opposing viewpoints are expressed with clarity and not without vigor.

The problem of the emulsion and of the image has been somewhat simplified since it has been shown[2] that silver bromide—and even bromoiodide in the

[1] *Trans. Farad. Soc.*, 19, 241 et seq. (1923).

[2] Trivelli and Sheppard, The Silver Bromide Grain, Monograph I. Eastman Kodak Lab., D. van Nostrand Co., 1921.

proportions met with in commercial plates and films—always crystallizes in the regular system. Even the finely divided halide occurring in process emulsions has been proved [1] by means of X-rays to be crystalline and of the same system. In fast emulsions, and even in some slow ones, the majority of the larger grains are flat tablets ranging in thickness from about $\frac{1}{14}$ to $\frac{1}{2}$ their average breadth.[2] A clump, or group of grains, may occasionally act like a single grain.

On the assumption of a single silver halide crystal as the fundamental unit of an emulsion, investigations soon led to the discovery, first by Svedberg[3], that more fundamental than the grains themselves are the "centers," the points in the grains from which development starts. It is on the nature of these centres that the sensitometric characteristics of an emulsion chiefly depend.

Toy [4] summarizes the main facts brought out by Svedberg, Slade and Higson, the Eastman Kodak Research Laboratory and the British Photographic Research Association investigations, with regard to the localization and distribution of the centers thus:

(1) They are distributed amongst the grains entirely haphazard, according to the laws of chance.

(2) On the average, they are distributed equally over the surface of spherical grains and are concentrated mostly on the edges if the grains are flat plates.

Mees [5] pointed out in 1915 that the grains in an emulsion are all of different sizes and that the sensitiveness and the plate curve will depend on the distribution of the different sizes of grains. It has been known for some time that, under apparently similar conditions, the plate with the coarser grain is usually the faster. Svedberg [6] showed, however, that with grains of approximately the same size, the same type of curve is obtained as with grains of assorted sizes. In other words, there can exist silver bromide emulsions built up of grains of equal size and shape but with different sensitiveness.

Toy [7] indicates the reasons for believing that the centers from which development commences are the actual points where the grain has been changed and that the centers therefore indicate the actual distribution of the material of the latent image. He summarizes the different views in the controversy as to how these centers are formed in the following:

(1) They are formed in homogeneous grains entirely by the light which is incident at points on the plate in finite discrete quantities.

(2) They are pre-existent in the grains before exposure as a chemically different substance, the function of the light being to change their condition

[1] Wilsey, *Phil. Mag.*, **42**, 262 (1921).

[2] Wightman, Trivelli and Sheppard, *Trans. Farad. Soc.*, **19**, 270 (1923).

[3] *Phot. J.*, **62**, 186 (1922); for additional references see *Trans. Farad. Soc.*, **19** (1923).

[4] *Trans. Farad. Soc.*, **19**, 290 (1923).

[5] *J. Franklin Inst.*, **179**, 141 (1915).

[6] *Phot. J.*, **61**, 325 (1921); **62**, 183 (1922). See also, Colloid Chemistry, Chem. Catalog Co. (1924).

[7] *Loc. cit.*, p. 291.

in such a way that they become capable of acting as reaction centers. The light is considered as incident equally on all grains.

(3) By a combination of (1) and (2). Heterogeneous radiation incident on grains containing specially light sensitive points.

Toy discusses these alternative theories thus:

(1) This is one view taken by Silberstein and others.[1] A detailed discussion of their work cannot be entered into here, and has already been made elsewhere. The theory is based on what we may call the extreme view of Planck's quantum theory of radiation—that proposed by Einstein in 1905. The developability of the grains is supposed to be completely determined by the chance of their being hit by one or more of the discrete light quanta which impinge haphazardly on the plate. In the paper to which attention has been called no reference is made to the discovery of the centers, the relations which are deduced as a consequence of the theory being concerned with the fraction of grains changed under certain conditions. In Toy's opinion, not one of the chief relations deduced is adequately supported by experimental evidence, and, as has been shown,[2] most of them are directly contradicted. Is the theory any better supported when considered in regard to the centers? If it were true that the grains were really subjected to bombardment by discrete "darts" of light, then, from what has been said before, the centers would of necessity represent their points of impact. Also, Silberstein in his second paper[3] says "due mention must be made of certain very valuable experimental investigations, since published by Svedberg, which seem again to corroborate the theory" (i.e., of light darts). Now, on the contrary, it seems to Toy that the topographical distribution of the centers is perfectly definite proof that the possibility (1) is untenable. For, if it were true, the centers would, on the average, be distributed equally over the projected area of spherical grains and not equally over the surface, and, in the case of flat plates, would be distributed equally over the surface instead of concentrated at the edges.

(3) Let us now turn to the third assumption, which is also being investigated by Silberstein and those working with him. The line of argument adopted in this modified form of the previous theory has recently been expressed by Mees[4] as follows: ". . . we are thrown back on the idea of differential sensitiveness among the grains, so that of the hundreds of quanta striking a grain only one may be considered to be operative, the rest falling upon insensitive portions of the grain." This idea certainly admits the existence of some kind of heterogeneity in grains, and thus, at first sight, it seems that it has more chance of success than its predecessor, but it is not difficult to see that it must also be untenable, as long as the inclusion of the "light dart" idea is maintained. One of the crucial tests which has been shown to fail for assumption (1) is this: Consider two beams of light of different frequencies, each monochromatic, incident on the grains, and let the intensity of each, as measured by a thermopile, be the same. Then, for equal times of exposure to each beam, the number of quanta received by the grains will be inversely proportional to the frequencies. Thus, for equal times of exposure of any emulsion to equal incident intensity of monochromatic blue light and monochromatic violet light, more quanta of blue than of violet will impinge on the grains. Provided then that the critical frequency is not exceeded, and all other conditions remain the same, the blue light should always give a greater percentage of grains changed than the violet. This will hold whether the whole of a grain or only part of it is sensitive to the light, and therefore provides a crucial test for possibility (3) as well as for (1). Toy has shown that the experimental evidence is in direct contradiction to this, a much greater effect being produced by the violet than by the blue.

(2) Though by the process of elimination we are driven back on (2) as the correct explanation of the formation of the centers, obviously such an assumption should be supported

[1] *Phil. Mag.*, 44, 257 (1922).
[2] *Phil. Mag.*, 45, 715 (1923).
[3] *Phil. Mag.*, 44, 956 (1922).
[4] *Nature*, 402 (1923).

by experimental evidence, and it must be capable of very severe tests from the chemical standpoint.

On this assumption, the extreme light sensitiveness of the grain is due primarily to the presence of some substance which is not silver bromide. Lack of space prevents a discussion of all the mass of evidence on the chemical side which has been accumulated in support of some kind of heterogeneous grain structure. The recent experiments of Clark [1] in the British Photographic Research Association laboratories are very important in this connection. He says: "If the sensitiveness of the halide grains is due entirely to the existence of a limited amount of special material in them, then, removal of this material should render the grains absolutely insensitive. On the other hand, if the sensitivity is due in part to the presence of a special substance, and in part to the silver bromide itself, it should be possible to reduce the speed of a plate to a certain minimum, i.e., to the speed of a pure silver bromide layer, by removal of the vital points." Clark has shown in this way that the sensitivity of a plate can be enormously reduced, though whether or not a definite minimum is reached is not yet established. He also found [2] that the centers were produced by exposure to sodium arsenite solution in exactly the same way as when the exposure was to radiation, and since he proved there is not interaction between sodium arsenite and silver bromide, we are forced to conclude that the latter is not the substance of which the center is composed.

The extreme light sensitiveness of the silver halide of the photographic emulsion is therefore primarily due in Toy's opinion to the presence of minute traces of some other substances.

Bancroft [3] is definite with regard to what the latent image really is:

"Owing to the very slight change in silver bromide on short exposure, it has always been popular to assume that the latent image is a physical or allotropic modification." Namias [4] assumed polymerization, Hurter and Driffield [5] depolymerization, Bredig [6] mechanical disintegration, Chapman Jones [7] labile form, and Bose [8] a mechanical strain. All these assumptions, and the further one of von Tugolessow [9] that the latent image is an oxidation product, are overthrown by the simple fact that all the phenomena of the latent image can be duplicated by immersing the plate in a solution of a weak reducing agent,[10] such as sodium arsenite. This proves that the latent image is some reduction product of silver bromide.[11] It cannot be a single, definite subhalide because no such compound has been prepared, because no satisfactory chemical reactions can be assigned to it, because the prolonged action of light does not yield the pure compound, and because this hypothesis cannot be reconciled with the facts of solarization.

The latent image cannot consist of a number of definite subhalides because we cannot isolate these in any way or give any definite proof of their existence

[1] *Phot. J.*, **63**, 230 (1923).
[2] *Brit. J. Phot.*, **69**, 462 (1922).
[3] *Trans. Farad. Soc.*, **19**, 249 (1923).
[4] *Chimie Photographique*, **102**, 110 (1902).
[5] *Phot. J.*, **22**, 149 (1898).
[6] *Eder's Jahrbuch der Photographie*, **13**, 365 (1899).
[7] Science and Practice of Photography, 383 (1904).
[8] *Phot. J.*, **26**, 146 (1902).
[9] *Phot. Correspondenz*, **40**, 594 (1903).
[10] Bancroft, *J. Phys. Chem.*, **14**, 294 (1910); Perley, *ibid.*, **14**, 689 (1910); Clark, *Brit. J. Phot.*, **69**, 462 (1922).
[11] Cf. Bancroft, *J. Phys. Chem.*, **17**, 151 (1913).

or properties, and because it is absurd to assume a number of definite subhalides between pure silver bromide and silver bromide containing an excess of 0.5 per cent silver when one can account for all the facts much better on the assumption of a phase of continuously varying composition. Trivelli [1] at one time postulated the existence of green Ag_8Br_7, blue Ag_8Br_6, yellow Ag_8Br_5, and red Ag_8Br_4; but nobody ever took these seriously and it is practically certain that Trivelli himself does not believe in them now.

The latent image cannot be free metallic silver (nucleus theory) because it does not show the chemical reactions of free metallic silver, because it does not show the electrical potential of free metallic silver, and because the hypothesis cannot be reconciled with the facts of solarization.

The latent image is due to silver adsorbed by silver bromide because it can be prepared synthetically, because it behaves like a phase of continuously varying composition, because this hypothesis enables us to account for all the chemical reactions of the latent image, and because this hypothesis enables us to account for the facts of solarization. The first suggestion that the latent image is due to adsorption was made by Carey Lea [2]; but this came before people were ready for it and the idea was really carried through by Lüppo-Cramer.[3] So far as Bancroft knows, this theory of the latent image is accepted pretty generally.

Hartung [4] has recently shown experimentally that thin films of silver chloride, bromide, and iodide lose weight when exposed in air to sunlight. This is due to loss of halogen, and the original weight is restored almost completely by rehalogenation. As was to be expected, the decomposition takes place much more rapidly in a vacuum.

[1] Cf. Luppo-Cramer, Das latente Bild., 23 (1911).
[2] *Am. J. Sci.*, (3) **33**, 349 (1887).
[3] Cf. *Kolloidchemie und Photographie*, 70 (1908).
[4] *J. Chem. Soc.*, **121**, 682 (1922).

CHAPTER XIX

INFRA-RED RADIATION IN CHEMICAL PROCESSES

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Since 1800, when Herschel first showed that a delicate thermometer having a blackened bulb evinced a rise in temperature when placed in the "dark" region beyond the red end of a visible spectrum, the cause and results of the existence of infra-red radiation have been of interest to both physicists and chemists. Succeeding work has shown plainly that such radiation is similar in character and general properties to ordinary visible light in that it is caused by a wave-emission at the velocity of light from a body oscillating with a definite frequency, and suffers absorption and reflection in a manner identical with visible light. The fact of its invisibility renders the demonstration of such properties more difficult than in the case of visible light; we shall see how such examinations are carried out and what bearing in general infra-red radiation has on chemical processes.

Limits of Infra-red: Those who are familiar with spectroscopic work in the visible region will realize that the limit of the visible red is by no means fixed, the visibility varying with the individual eye. In defining the limits of the infra-red region, therefore, it is only possible to give an average result. The visible portion of the spectrum is usually taken as extending from 0.4 μ to 0.8 μ but recent work [1] has shown that 0.75 μ and in a few cases 0.77 μ is the longest wave-length to which the average eye is sensible. It may be assumed, therefore, that from a wave-length 0.75 μ onwards constitutes the infra-red spectrum. A definite limit, however, is not at all necessary, since the usual methods adopted for measuring infra-red rays are also capable of detecting visible and even ultra-violet rays, and data of an infra-red spectrum may quite well be given from 0.7 μ onwards.

On increasing the wave-length from this point, one continues to pass through similar waves, and, up to the present, measurements have been obtained at a wave-length of 314 μ.[2] It is only as a result of experimental difficulties that no longer wave-length has been reached. It has been shown that Hertzian waves, familiar now in wireless telegraphy, are precisely similar to the waves producing visible and infra-red radiation. The shortest wave-length of these electrical radiations so far detected is of the order of one milli-

[1] Coblentz, *Bull. Bur. Stands.*, **14**, 167 (1919). Hyde and Forsythe, *Astrophys. J.*, **42**, 285 (1915).

[2] Rubens and von Baeyer, *Phil. Mag.*, **21**, 689 (1911).

meter, that is, 1000 μ, and, since there is no apparent reason for a discontinuity in the series, in view of the results already obtained in other spectroscopic regions, it is reasonable to surmise that the limit to the infra-red radiation of extremely long wave-length has not so far been reached. Of the known wave-lengths, those up to 10 μ lie in the short wave infra-red region, whilst beyond 10 μ the region is known as the long wave infra-red region. Such a distinction is convenient as will be seen later from the fact that each region has its own particular properties from the point of view of chemical constitution and reaction.

Sources of Infra-red Radiation: One of the earliest investigations in infra-red measurements was made by Langley [1] in his study of the solar spectrum. As a general source of infra-red radiation, the difficulties of focussing the sun in a constant direction, coupled with its rather weak and ever-varying intensity due to atmospheric conditions, render it useless for spectrum work. For total radiation work, where a certain region may be isolated by light filters, the sun forms a convenient source.

The incandescent gas mantle was used as a source of infra-red rays by Nichols and Rubens [2] in their study of the absorption, refractive indices, and residual rays from rock salt and sylvine. Later, a Linnemann zircon burner was substituted for the ordinary gas mantle, and, still more recently, Rubens and von Baeyer (*loc. cit.*) examined the emission from quartz mercury lamps and various metallic arcs. All these sources and more especially the latter are extremely strong in the very long wave radiation but are of comparatively little use in the short wave region.

The Nernst lamp and heater is a particularly useful source for wave-lengths between 1 μ and 5 μ. It can be used up to about 20 μ, but beyond 8 μ the intensity falls off rapidly and measurements become less precise. The advantage of the Nernst lamp over a carbon arc, which also burns in air and requires no cover like electric filament lamps, lies in its constant intensity. Using an accumulator battery giving a constant current, a Nernst lamp fitted with an iron-wire resistance lamp in series can be maintained constant without attention, provided the lamp is protected from draughts. The carbon arc, on the other hand, though of stronger intensity, cannot be maintained constant owing to sputtering of the arc even when automatically fed, and is thereby useless for infra-red spectrum work.

In the very short wave-length region, an ordinary nitrogen-filled tungsten lamp may be used. The glass covering of the lamp absorbs very little, whilst with a quartz cover such a lamp is extremely constant in intensity and useful up to 4 or 5 μ.

The efficiency of any source of radiation for a given purpose, however, will depend entirely on the delicacy of measurement which may be obtained for registering such radiation. The Nernst lamp, for example, which has a maximum intensity between 2 and 3 μ, depending on the composition of the

[1] *Phil. Mag.*, (5) **17**, 194 (1884).
[2] *Ann. Physik*, **60**, 402 (1897).

filament, is generally used as a source in this region, although Rubens has obtained readings at 60 μ, using very delicate measuring instruments. Nevertheless, in general, it is more useful to restrict a given source of radiation to a given region in the manner pointed out above, unless measurements are being made over a wide range, necessitating the use of the same source throughout, which normally would cover the efficient regions of two different sources.

Measurement of Infra-red Rays

Methods of Analysis: The point of primary importance in the analysis of infra-red radiation is that, as a rule, it is practically impossible to use a diffraction grating alone, owing to the overlapping of the spectra of different orders. Gratings have been used, however, in conjunction with prisms, a good example being that due to Langley (*loc. cit.*). A grating with 18,050 lines, 142 to the millimeter on a spherical mirror 1.63 meters focus, was used. The Fraunhofer line D_2 of the third order spectrum was focused on the slit of the measuring instrument when there was also present, by the theory of the grating, 0.888 μ of the second order spectrum and 1.767 μ of the first order spectrum. By interposing a prism in this beam, these lines were refracted at different angles which could be calculated, and could be measured at their respective positions. The work is tedious, however, and subject to much experimental error.

Another method of using a grating is that adopted by Rubens (*loc. cit.*) in the Reststrahlen method where all other wave-lengths than the one desired could be suppressed. The grating employed was a transmission grating of silver wire 0.1858 mm. diameter and the same spacing. The rays from the grating were successively reflected from four or five blocks of quartz, rock salt or sylvine, the final ray being then found to be practically monochromatic, the other rays having been absorbed by the blocks and not reflected. In this way, Rubens found what wave-lengths were selectively reflected from many substances and, therefore, what wave-lengths were absorbed by the substances, the advantage of the method being that absorption data were obtainable indirectly at positions where direct observation was impossible. The figure 314 μ previously quoted as being the longest wave-length so far measured was obtained in this way, using rock salt blocks, showing that rock salt absorbs at this position, a fact which could not be obtained by the ordinary spectroscopic methods used in the infra-red.

A special type of grating known as the echelette [1] grating has been made on gold-plated copper surfaces, the rulings of which are so large as to make a certainty of the exact form of the groove. Using such an echelette with only 1000 lines to the inch, Wood has shown that the emission band for carbon dioxide from a bunsen burner, found by others at 4.40 μ, is directly observed and is resolvable into two maxima at 4.30 μ and 4.43 μ. The dispersion of such gratings is said to be nearly seventeen times that of rock salt and four times that of fluorite in the region between 4 and 5 μ.

[1] Wood, *Phil. Mag.*, **20**, 770 (1910). Trowbridge and Wood, *ibid.*, **20**, 886 (1910).

On account of this overlapping with ordinary ruled gratings it has become the rule to use prisms of substances which do not absorb infra-red rays and yet have good dispersive power. Prisms of rock salt, sylvine, fluorspar and quartz are the most frequently used. Fluorspar becomes practically opaque to radiation of wave-length 11 μ, whilst rock salt and sylvine transmit as far as 20 μ and 25 μ respectively. Quartz, on the other hand, which possesses strong absorption bands at 3 μ, 8 μ and 21 μ and is thus opaque to comparatively short wave-lengths, is very transparent for wave-lengths in the region of 50 μ. Up to about 20 μ, therefore, a prism of rock salt which gives good average dispersion is the more usual analyzer used, whilst beyond this point quartz will be found more suitable.

As in a spectroscope used for visible light the collimated beam is focused on to a glass prism and from the prism into the eyepiece by glass lenses, so also may the infra-red rays be treated by using a prism and lenses made of rock salt.[1] The drawback to this arrangement is the doubled or trebled absorption by the rock salt of the rays passing through the spectroscope and the consequent weakening of the radiation in the beam finally emitted. As a result, the method now universally adopted is to focus the rays by means of highly polished concave metallic mirrors. Measurements of the reflectivity of infra-red radiation by various metals have aided the choice of suitable metals to be employed. Platinum, electrodeposited on a glass surface, on account of its resistance to the action of the atmosphere and high reflective power, is now in frequent use.

Instruments of Measurement: The measurement of radiant energy, more especially in the infra-red region of the spectrum, is a difficult and somewhat tiresome proceeding, demanding extreme care and patience on the part of the investigator. The fact that such radiation is usually from surfaces, the temperature of which cannot be obtained, necessitates its transformation into other forms of energy, the effects of the latter being then measurable. Such a receiver, however, being subject to losses of energy by conduction within itself, by reflection and radiation from its surface and by convection round its surface, can hardly be expected to yield results of precision without much care being paid to these points.

Various instruments of this kind have been devised wherein the infra-red radiation is received and converted into another form of energy, being measured as such in some units. It is impossible in the scope of this chapter to give details of the construction of all such instruments. The works of Coblentz [2] must be referred to for more particular detail, where an excellent treatment is given of the comparative merits of the various instruments. Let it suffice that some of the more important instruments are mentioned and the mode of operation given.

Microradiometer: The microradiometer was one of the earliest instruments devised, but has now been superseded by more delicate types of receivers. It consists of a narrow glass capillary tube, containing, in the center, a drop of

[1] Langley, *Brit. Ass. Rep.*, p. 465 (1894).

[2] Coblentz, *Bull. Bur. Stands.*, **4**, 391 (1907–8); **9**, 7 (1913).

mercury in a solution of zinc sulphate in water, into which dip two platinum electrodes. The ends of the tube widen out into bulbs containing air or a gas with a high coefficient of expansion, the bulbs being closed with rock salt windows. In use, the instrument forms part of a Wheatstone bridge circuit. On exposure to infra-red rays, the gas expands, driving the column of liquid away and thereby affecting the resistance between the platinum electrodes and producing a deflection in a delicate galvanometer. Such an instrument can be made very sensitive but is more adaptable to total radiation from a body than to more particular spectral analysis.

Bolometer: The bolometer is simply a Wheatstone bridge, two arms of which are made of very thin blackened metal strips of high electrical resistance and high temperature coefficient, one or both being exposed to the radiation. When thus exposed, their temperature changes, which unbalances the bridge and causes a deflection in the galvanometer, corresponding to the amount of energy absorbed. The sensitivity of the bolometer depends, therefore, on that of the galvanometer and, for the moving coil type, a gain in the sensitivity has the drawback of an increase in the period of the deflection. Langley (*loc. cit.*) was one of the first to use a bolometer, his instrument being so sensitive that a rise in temperature of less than one millionth of a degree Centigrade produced a readable deflection in the galvanometer.

Thermopile: The formation of an electrical current when the junction between two metals is heated has given rise to the thermopiles in general use today. The more usual types consist of about twenty junctions between iron and constantan, or bismuth and silver wires, blackened to receive the infra-red rays. The multiple effect of such a series of junctions gives rise to a small electrical current which is directly measurable on a delicate galvanometer. Coblentz has developed some extremely sensitive piles for use both in air and in vacuo in which latter he finds the sensitivity increased three or four times. Johansen [1] also gives details of a vacuum thermopile, using iron and constantan junctions.

The instruments mentioned so far have necessitated the use of delicate galvanometers. Of the many types in use mention may be made of the Paschen, Broca and Thomson galvanometers. The former have a moving magnet system whilst the latter is a moving coil galvanometer. Such instruments have to be free from external vibrations, of fairly short period and shielded from stray magnetic effects. The attainment of good experimental results is only realized by one experienced in the removal of such difficulties, and it is with a view to removing the necessity of such galvanometers that the radiomicrometer and radiometer have been developed.

Mention may be made in passing to the use of the thermionic triode valve and telephone in place of the galvanometer. By placing an electrically controlled wire dipper in a mercury cup in the thermopile circuit and passing the interrupted current through a step-up transformer to the valve-telephone receiver, delicate audible records may be obtained due to the amplification.

[1] *Ann. Physik*, **33**, 517 (1910).

Bellingham [1] points out that this method is more delicate than a galvanometer, is unaffected by vibrations or magnetic fields and is instantaneous in action, a point quite unattainable even in the most dead-beat galvanometers.

More recently Dr. Moll in Holland has devised a thermopile and galvanometer of extreme sensitivity and very great utility. The outstanding feature of the pile is its very small heat capacity, ensuring rapidity of action without loss of sensitivity. Thus, in Rubens' thermopile, more than 15 seconds were required for the current due to constant radiation to reach its final value, whilst any attempt to decrease this period was made at the expense of sensitivity. The Moll piles consist of thin strips, each consisting of two strips of different metals joined end to end and soldered at the other ends to copper bars. Such strips may be exposed along their whole length and, by reason of the difference in heat capacity between the junctions which rest on the copper bars and the middle junction, the latter, when irradiated, attains a much higher temperature than the others, while the high conductivity between the junctions and the small heat capacity of the middle junction cause equilibrium of temperature to be reached very quickly.

The Moll galvanometer used in connection with these piles has a coil of about 64 ohms resistance moving in an electromagnetic field actuated by 1 to 1.5 amps. at 4 volts. The instrument is extremely quick in action, having a period of approximately one second, and is very sensitive. The deflection per microampere with scale at one meter distance is over 200 mms. The build of the electromagnetic coil is so heavy that the usual earth tremors and building vibrations do not affect it at all, whilst the constancy of zero may be shown by the fact that after a ten minutes deflection of 200 mms. the creep is less than 3 mms.[2]

Radiomicrometer: The original instrument as used by Boys and by Paschen [3] consisted of a very small bismuth-silver thermocouple connected in series with a loop of copper or silver wire suspended in vacuo between the poles of a fixed magnet, the weight of the whole suspension being from 10 to 15 milligrams. On exposing the thermocouple to radiation, the junction becomes heated, causing an electrical current to flow through the wire loop, which is immediately deflected in the magnetic field. In this simple state, although not susceptible to extraneous electrical or magnetic effects, the lightness of the suspension and its sensitivity render it liable to outside radiation effects as well as vibrations, causing a poor zero reading. Great improvement was afforded by H. C. Jones [4] who added a second thermocouple, identical with the first but connected in opposition with it. External heat effects then affected both couples simul-

[1] *Nature*, **111**, 534 (1923).

[2] This new combination of thermopile and galvanometer goes far on the way to a solution of most of the problems which are encountered in infra-red work, and is to be recommended strongly, especially to those new to the work, who are inexperienced in the usual difficulties to be overcome in other instruments. The manufacture of these instruments is in the hands of the Cambridge and Paul Scientific Instrument Company, London.

[3] *Ann. Physik*, **48**, 272 (1893).

[4] *J. Am. Chem. Soc.*, **37**, 776 (1915).

taneously, the net effect being zero. For use with an infra-red spectrometer, radiation was only focused on one element, the second being temporarily out of action. Unpublished work of the author, however, has shown that the element exposed under such conditions acts itself as a radiator, affecting the auxiliary couple and consequently causing incorrect readings. The extent of this effect is small but nevertheless is sufficient to affect the accurate determination of intensities.

Radiometer: The principle of the radiometer differs entirely from that of any of the above instruments in that it is not electrical in nature. Two small strips of blackened mica or platinum, of about one or two milligrams weight each, balance one another vertically about a fine glass rod, from two to three centimeters long, to which is attached also a small mirror, the whole suspended by a quartz fiber. The suspension is enclosed in a convenient receptacle which can be exhausted to a very high vacuum. On exposing one of the vanes to radiation by means of a slit, the vane becomes warmed and the traces of air which remain in the instrument bombard the surface more violently and cause it to be deflected. The deflection, too, is partially due to the light pressure on it. The sensitivity depends on the lightness of the suspension and fineness of the quartz fiber, and on the vacuum in the instrument. A critical point is reached on exhausting after which, on further decreasing the pressure, the sensitivity also decreases.

The radiometers as used by Nichols [1] and Coblentz [2] were extremely sensitive instruments but had long periods and were consequently very slow in working; they were susceptible to the slightest vibration, necessitating an isolation from all possible mechanical vibrations during the course of an investigation. One of Coblentz's radiometers, however, which possessed a heavier suspension, though not being quite so sensitive, was nevertheless capable of being used under quite ordinary conditions, and it would seem that, with care, one could assemble a radiometer to suit any given conditions.

Such instruments as the radiometer and radiomicrometer must necessarily be built up by the investigator, as the instruments generally on the market do not in any way approach the sensitivity required in infra-red work and it is probably for this reason that greater use has not been made of them, especially the radiometer, which is undoubtedly the most sensitive instrument obtainable.

Photo-electric Cells: More recently, the change of resistance of selenium on exposure to light has been used as a means for measuring radiation, but, since the maximum sensitivity occurs only in the near infra-red, selenium cells are only adaptable for special limited portions of the spectrum. The same applies to the potassium and potassium hydride photoelectric cells,[3] which are more useful in the visible and ultra-violet than in the infra-red region. Coblentz [4] finds that the thalofide cell, that is, a cell containing thallium oxysulphide, is

[1] *Ann. Physik*, **60**, 402 (1897).

[2] Investigation of Infra-red Spectra, *Carnegie Inst. Pubs.*, **35** (1905), **65** (1906), **97** (1908).

[3] Coblentz, *Bull. Bur. Stands.*, **14**, 512 (1918–19).

[4] Coblentz, *Bull. Bur. Stands.*, **16**, 253 (1920).

sensitive up to 3 μ and may conveniently be used in this region as a general measuring instrument. Such cells are worked in conjunction with a delicate galvanometer, the cell forming one arm of a Wheatstone bridge, which becomes unbalanced by a change in resistance in the cell on exposure.

Photography: In concluding these methods of registering radiation the applicability of photography to the infra-red region should be mentioned. One of the earliest attempts at infra-red investigation was made by Abney and Festing [1] who used photographic plates in which the silver bromide emulsions in the collodion appeared red by transmitted light. Data were obtained up to 1.2 μ and in some cases even to 2 μ, though subsequent attempts to reproduce similar effects have failed.

Using dicyanin as a sensitizer on ordinary panchromatic plates, Meggers [2] obtained the spectra of various metallic arcs to 0.9 μ and the solar spectrum to 1.0 μ. The spectral detail attainable by photographic means makes it far superior to any other mode of examination. It is limited, however, in range, as shown, but serves to give exceedingly valuable information in a region where the dispersion is small. The numerous bands obtaining in this region are difficult to detect by other radiometric means. The importance of this region will be seen later in discussing the relations between absorption spectra and chemical reaction.

Calibration of Spectrometer: The determination of the wave-length of a particular ray emerging from an infra-red spectrometer depends on the type of instrument used. In calibrating a spectrometer which employs a grating to spectrolyze the radiation, the size of the rulings and the angles of diffraction at the grating will give at once the wave-lengths emitted. With a prism, however, the calibration is more difficult. The first method used was an interference method due to Mouton.[3] The work of Rubens and Paschen (*loc. cit.*) has now given us very accurately the indices of refraction of rock salt, sylvine, quartz, namely, those substances which are generally used for prisms; consequently, the wave-length of the rays from such prisms may be calculated for a given angle of emergence of the ray.[4]

Since, as a rule, the receiving instrument must remain stationary, the successive portions of the spectrum are projected thereon, by rotating the prism, maintaining the latter at constant deviation by means of a mirror-prism device described by Wadsworth.[5] The prism may then be rotated by a drum-head on which is calibrated directly the wave-length of the ray emerging at any given position. That the receiving instrument is then correctly situated relative to the spectrometer is determined by observing such a definite band head as the 4.40 μ emission band for carbon dioxide in the following way. The deflections given by the receiving instrument, which has been set approximately in position relative to the spectrometer, of the radiation from a Hefner

[1] *Phil. Trans.*, **172**, 887 (1882).
[2] *Bull. Bur. Stands.*, **14**, 371 (1918–19).
[3] *Ann. Chim. Phys.*, (5) **18**, 145 (1879).
[4] Cf. Coblentz, Part 1, *Carnegie Inst. Pub.* No. **35** (1905).
[5] *Phil. Mag.*, (5) **38**, 346 (1894).

lamp burning amyl acetate or from a bunsen burner, are taken for several wave-lengths around 4.40 μ. These deflections on plotting against wave-length should exhibit a maximum at 4.40 μ. If such is not the case, the receiving instrument is moved slightly until, finally, the emerging ray from the spectrometer is focused centrally on the receiving plate of the receiver, as evidenced by the correctness of position of the observed emission band.

With such an arrangement of spectrometer and measuring instrument, one is then in a position to measure the quality of infra-red radiation from various sources in precisely the same manner as that just given. Plotting the deflections against wave-length, a smooth curve is obtained which exhibits certain maxima and minima, from which a comparative knowledge is obtained of the emission at various wave-lengths of the source of radiation employed. Such emissive intensities are not in absolute units, but depend on the receiving instrument employed. It is possible, however, knowing the absolute sensitivity of the instrument used, to give such intensities in absolute units. We shall see later that such is seldom necessary as comparative methods are usually employed.

If, now, a cell holding a liquid be interposed between the source of radiation and the spectrometer, and the deflections at various wave-lengths are again taken, the resulting curve no longer resembles that previously obtained, due to the absorption by the liquid at certain wave-lengths. The data so afforded depend on the intensity of the source of radiation at the various wave-lengths and do not give absolute measures of the absorption. If the intensity of the source were known in absolute units, the true absorption could be calculated. As previously mentioned, a comparative method offers a solution of the problem more easily.

Infra-red Absorption Spectra

Let us consider at the outset somewhat theoretically the method of observing absorption spectra in the infra-red. Coblentz observes the intensity, as measured by the deflection of his measuring instrument, of the radiation passing through either a rock salt plate or a cell made up of two rock salt plates, each of which is half the thickness of the first plate, the cell containing the substance under investigation. The ratio of these two transmission intensities is taken as the fractional transmission of a thickness of the substance in the second cell. H. C. Jones (*loc. cit.*) points out that, by using a "differential method," that is, by comparing two cells each containing the same substance to be examined but of different thicknesses, corrections for reflection at the outer surfaces of the cells and also for the difference in the refractive index of cell wall and substance examined are eliminated. Coblentz,[1] on this point, states that the loss of energy by reflection or absorption of cell wall is uniform up to 2.4 μ, but he employs the method as far as 10 and 15 μ.

Comparing two cells, containing the substance under investigation, of different thicknesses d_1 and d_2, the intensity of the incident light I_0 is related

[1] *Bur. Stands. Sci. Papers*, No. **418** (1921).

to that emitted after passing through each cell by the ordinary absorption equations, namely:

$$I_1 = I_0 \cdot e^{-kd_1},$$
$$I_2 = I_0 \cdot e^{-kd_2},$$

where k is the absorption coefficient of the substance. The effective thickness of substance examined is, however,

$$d_1 - d_2 = d.$$

Hence, the intensity of radiation emitted by a thickness d is

$$I/I_0 = e^{-kd} = e^{-k(d_1-d_2)},$$

which, from the above equations, is seen equal to I_1/I_2. Hence, we have:

$$I/I_0 = I_1/I_2,$$

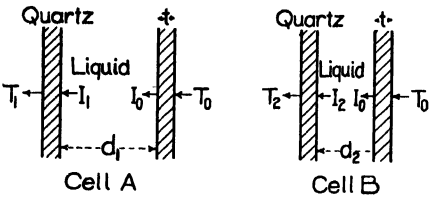


FIG. 1

that is, the ratio of the intensities of radiation transmitted through two different thicknesses of substance is equal to the fractional transmission of a thickness which is the difference between the two thicknesses examined. Up to this point, only the actual substance in the cell has been considered. It is necessary to consider also the effect of the cell walls on the transmissions.

Consider two cells A and B, as shown in Fig. 1, each consisting say of two quartz plates of equal thickness enclosing a certain depth of liquid. Let T_0 be the intensity of the incident light, the same in both cases. On meeting the first quartz plate T_0 suffers some reflection from the quartz-air surface, again identical in the two cases. In passing through the quartz plate there is some absorption by the quartz, and at the quartz-liquid surface again a reflection, which, since the plates are both the same thickness and the surfaces of reflection are the same in the two cells, will not differ one from the other. The intensity I_0 of the light actually incident on the liquid is therefore the same in both cells.

Let I_1 and I_2 be the intensities of the light after passing through the liquid in A and B respectively, and T_1 and T_2 the final emerging rays. In going from I_1 to T_1, and from I_2 to T_2 there is again a reflection at the liquid-quartz surface, an absorption by the quartz, and a reflection at the quartz-air surface.

At the first reflection I_1 suffers a decrease fractionally proportional to its intensity. Denoting this fraction by x, the intensity after the first reflection becomes:

$$I_1 - xI_1 = I_1(1 - x).$$

The subsequent absorption by the quartz follows the above absorption law,

giving as emerging intensity

$$I_1(1 - x)\cdot e^{-at},$$

where a is the coefficient of absorption of quartz and t is the thickness of the quartz plate.

At the last reflection at the quartz-air surface there is again a fractional decrease, say y, of the incident intensity. The final intensity T_1 is therefore given by

$$T_1 = I_1(1 - x)\cdot e^{-at}\cdot(1 - y).$$

For cell B, in a similar manner, we have

$$T_2 = I_2(1 - x)\cdot e^{-at}\cdot(1 - y),$$

since the fractional decreases due to reflection depend wholly on the surface, which is identical in the two cells, and the quartz plates are the same thickness throughout. Whence it follows that

$$I_1/I_2 = T_1/T_2,$$

that is, the ratio of the intensities of the radiation finally transmitted from the cells gives the fractional transmission, and therefore the percentage transmission, of a thickness of liquid which is the difference in thickness between the two cells examined.

Strictly speaking, then, any other method than the comparison of two different thicknesses of the same substance is inaccurate, in that the reflections in the two cells will not be identical. The work of Coblentz, however, would show at least that, for mere identification of position of a band head, the other method suffices. Nevertheless, on attempting to deduce a value for the absorption coefficient k in the above expressions, the values of the fractional transmissions are not found to yield a constant which is independent of thickness, as should be the case from the expression.

Incidentally, it may be mentioned that unpublished work by the author shows that the determination, with a reasonable degree of precision, of the absorption coefficient of a liquid such as water, benzene or heptane, in the short infra-red region is one of the greatest difficulty, owing to the enormous heating effect, due to the large physical absorption, which occurs in an extremely thin layer on the exposed side of the liquid. In fact, the only satisfactory mode of working is to renew the liquid rapidly during exposure. This matter of temperature control would appear to be of greater account in the "differential method" of observation than in the method used by Coblentz, because, in the former case, one compares two cells of different thickness and therefore of different heat capacity which would give rise to different temperatures in the two cells and hence to transmission intensities which are not truly comparable. Coblentz, on the other hand, could utilize this effect in maintaining such a body as phenol as a liquid during a complete examination from

1 μ to 7 μ whilst at the same time obtaining transmission data for the phenol, which was at approximately the same temperature throughout.

We are now in a position to give a definite practical method for determining the absorption spectrum of any body. Let us assume, for convenience, that we wish to plot the absorption spectrum of nitrobenzene, using a radiometer as measuring instrument. First, two cells are constructed which are virtually small boxes possessing quartz windows having an inlet and outlet through which the liquid passes continuously during the examination. The distance between the windows in each cell gives the thickness of the cell, that is, the thickness of the layer of liquid examined. The cells are mounted on a carrier immediately in front of the radiometer window. By means of suitable stops the cells may be brought in turn before the window in exactly the same position throughout the run. With the cells in this position, the light passing through them is practically monochromatic, having already passed through the spectrometer. The heating effect is thereby greatly reduced from what it would have been had the cells been exposed to the full radiation of the source before being analyzed by passing through the spectrometer.

It must be noted that the sensitivity of the receiving instruments previously mentioned is so great that it is imperative for precise observation to take readings at a distance of about eight feet from the apparatus, preferably enclosing the instruments in a small room with an observation window, or taking observations through a large glass screen as a precaution against the heating effect of the body.

The source of radiation is separated from the spectrometer by a water-cooled shutter which can be raised when required by means of a cord running to the observer behind the screen. The deflections of the radiometer are taken by observing, with an illuminated scale and telescope, also behind the screen away from the instruments, the reflection of the scale in the mirror in the radiometer. The prism is then set at a certain wave-length and the deflection for one cell observed by noting the zero of the radiometer through the telescope, raising the shutter and thereby exposing the cell, and noting the maximum deflection obtained. This is repeated three or four times. The cells are then interchanged by sliding the carrier along, and the process repeated for the second cell at the same wave-length. The ratio of the mean of these readings gives the fractional transmission at that wave-length. By repeating these observations at frequent intervals throughout the region to be examined, a series of transmissions are obtained which, on plotting graphically against wave-length, gives a transmission curve or, what is almost identical, an absorption curve. A typical example is shown in the graph in Fig. 2. The curve is for a layer of net thickness 0.2686 cm. of nitrobenzene from 0.8 μ to 3.4 μ. From the curve, one observes that nitrobenzene absorbs to differing extents at positions 1.0 μ, 1.4 μ, 1.7 μ, 2.8 μ and 3.25 μ.

The question naturally arises as to what is the cause, and what the mechanism of such absorption? It was with a view towards the elucidation of this problem that Coblentz made his extensive investigations into infra-red absorption spectra. Having pointed out that emission spectra generally imply

a high temperature and therefore an uncertainty of the composition or constitution of the radiator, the absorption spectra as ordinarily measured at room temperatures will correspond to a constitution of which we have full knowledge. Although, in gases, the molecules have a greater free space in which to vibrate, yet, even in highly complex organic bodies, it is possible for single groups of atoms in the molecule to exhibit the natural frequencies which they would have in simpler bodies.

With this end in view Coblentz examined the absorption spectra of over 130 organic compounds up to 15 μ. They include solids, liquids and gases and belong to all the principal groups of organic compounds. The work of previous investigators,[1] which need not be considered here, was repeated and extended, whilst corrections were made where obvious errors had occurred.

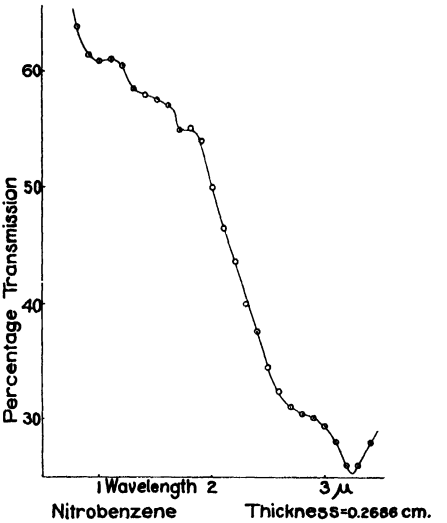


FIG. 2

From a study of isomeric as opposed to stereoisomeric compounds, Coblentz showed that the arrangement of atoms in the molecules, that is, the structure of the molecules, has a great influence on the absorption, in contrast to the spatial configuration which has no effect. Thus, dextro and lævo-pinene have identical spectra. Various subgroups were found to have particular bands, for example, the amino and methyl groups at 2.96 μ and 3.43 μ respectively. The occurrence of harmonics in the band positions of various compounds was pointed out. Thus, in bodies exhibiting the effects of a methyl group, maximum absorption occurs at 0.84 μ, 1.70 μ, 3.43 μ, 6.8 μ, and 13.6 μ. The effect of the ortho, meta and para disubstitution of benzene was studied, showing the dissymmetry of the ortho compounds and increased symmetry up to para compounds, by a larger shifting of the head of the benzene band at 3.25 μ towards the longer wave-length by the former than by the latter.

Coblentz finally concluded that the source of absorption bands in the infra-red is a "nucleus" or "ion" within the molecule, but refrains from identifying definitely between any certain group and the "ion." The more recent advances made on the constitution of the atom and the molecule have led to the observation that the atoms within the molecule are the cause of infra-red

[1] Ångstrom, *Ofversigt. af. Kon. Akad. Forhandl. Stockholm*, Nr. 7 (1890). Julius, *Verhl. Kon. Akad. Amsterdam* (1892). Paschen, *Ann. Physik*, **53**, 336 (1894). Krüss, *Z. physik. Chem.*, **2**, 372 (1888), *ibid.*, **18**, 559 (1895). Ransohoff, *Diss. Berlin* (1896). Rubens and Aschkinass (inter alia), *Ann. Physik*, **64**, 584 (1898). Puccianti, *Nuov. Cim.*, **11**, 241 (1900).

absorption, whilst the electrons in the atoms are revealed only in the ultra-violet region.

The ideas set afoot by Coblentz's work have been greatly advanced recently in the hands of Henri [1] and Baly,[2] working independently on the problem of absorption spectra and chemical reactivity. Whereas, in Coblentz's work, the spectra were restricted to the infra-red only, Henri and Baly have extended the relations to absorption in the visible and ultra-violet regions. From a study of 240 bodies, chiefly organic, Henri shows that it is possible to obtain some idea of the mechanism of molecular structure from a study of absorption spectra. He claims to have shown that there is a strict relationship between the positions of absorption in the ultra-violet and infra-red regions, namely, that the former are integral sub-multiples of some fixed infra-red wave-length in the absorption spectrum of that body; where there is more than one infra-red band, the ultra-violet bands are the same integral submultiples of them. From this he concludes that the molecule is composed of vibrators varying in size from that of the electron to that of the molecule as a whole and that their separate motions are interdependent in much the same manner as the wheels of a clock depend one upon the other. Such a view of the molecule offers a reasonable explanation of the mechanism of physical absorption whereby a body becomes heated. Any absorption which does not go towards producing chemical reaction provokes within the molecule movements of other vibrators at a lower frequency. This will proceed until the final vibration corresponds with the far infra-red frequencies, and it is these vibrations which heat the body.

From these conclusions, Henri proceeds to demonstrate with remarkable accuracy how it is possible to calculate the absorption spectra from a knowledge of the constitution of a body and vice versa; he finally concludes that the stability of a body may be measured by the energy necessary to decompose a molecule, which energy may be measured from the absorption of the body.

Whereas Henri arrived at these conclusions from a purely practical point of view, Baly attempted a more theoretical theory of absorption, fluorescence and phosphorescence, with much the same results. The theory is developed along two lines. First, the electromagnetic fields surrounding the atom, as used by Humphreys to explain the Zeeman and pressure-shift effects, are applied to molecules. The separate existence of such atoms in the molecule must be metastable and the electromagnetic force fields will condense with the escape of energy. A molecule in which the atomic fields are fully condensed will be extremely stable and show no reactivity. Such closed fields can be opened to promote reaction either by other molecules possessing residual affinity, that is, only partially closed fields, such as solvents, or by the action of light which is selectively absorbed. Obviously, there will be definite equilibria between the closed fields of the molecule and the partially closed ones of the solvent. Such stages will be characterized by a definite absorption. The light absorbed is emitted sometimes as infra-red and at other times as

[1] Photochimie, 1919.

[2] *Astrophys. J.*, **42**, (1) 4 (1915).

visible or ultra-violet, when fluorescence or phosphorescence is manifested. These latter, therefore, mean energy emission at a frequency also characteristic of the molecular system. Experimental proof is afforded by the existence of intermediate stages in chemical reactions, by the variation of absorption with progressive dilution and by the fact that the fluorescence emission of certain organic compounds in one solvent has the same frequency as the light absorbed by the same compound in a different solvent.

Combining these observations with the work of Bjerrum [1] on rotational frequencies, Baly deduces the integral relationships also found by Henri and shows, too, that the absorption spectra may be calculated from the molecular frequencies which, according to Bjerrum, may be obtained directly from the moment of inertia of the molecule.[2] The conclusions of Baly would therefore seem to be more theoretical than those of Henri, though the practical confirmation of the theory in the latter case would also confirm Baly's views.

Shaefer and Schubert [3] whilst examining the reflection, as opposed to the absorption spectra, of various solid carbonates and sulphates up to 20 μ, find that the infra-red properties of these bodies may be deduced from their optical behavior in the visible and, since such properties as dispersion and double refraction depend only on the electronic vibrations and therefore on the ultra-violet frequencies, they conclude that there must exist some relation between the infra-red and ultra-violet.

Such relations between ultra-violet and infra-red would seem to imply some connection between the electronic, atomic and molecular vibrations and rotations, as would also be the case from the semi-empirical relation due to Haber.[4] His relation connects the characteristic infra-red frequency, ν_r, that is, the frequency of the residual ray which is capable of accounting for the specific heat of the substance, and the characteristic ultra-violet frequency ν_v which corresponds with the maximum of the selective photoelectric effect, in the following way:

$$\nu_r/\nu_v = \sqrt{M/m},$$

where m is the mass of the electron and M is the molecular weight of the substance. A discussion as to the significance of M is given by Lewis [5]; in general, good agreement is to be found between the results experimentally observed and those calculated from the above expression.

Such ideas of a definite relation between the various vibrations occurring simultaneously in a molecule would not in general appear necessary from the present point of view of the structure of the molecule. There would therefore seem to be some inconsistency between the two, which requires further elucidation.

[1] *Z. Elektrochem.*, **17**, 731 (1911); **18**, 101 (1912).
[2] Eucken, *Verh. deut. physik. Ges.*, **15**, 1159 (1913). von Bahr, *ibid.*, **15**, 731, 1154 (1913).
[3] *Ann. Physik*, **50**, 283 (1916).
[4] Haber, *Verh. deut. physik. Ges.*, **13**, 1117 (1911).
[5] *J. Chem. Soc.*, **111**, 1086 (1917).

A further example of the work done in the short infra-red region is that due to H. C. Jones [1] and co-workers, which comprises an examination of the infra-red absorption coefficients of a number of inorganic salts in various solvents. The investigation bore in a general manner on the concept of solution and the theory of solvation advanced by Jones. The region covered in the investigation was from 0.6 μ to 1.3 μ. Determinations were made of the absorption of water and five simple alcohols as solvents, and salts of cobalt, nickel, iron and chromium in those solvents, as solutions, using a grating spectrometer and radiomicrometer. The similarity of position of maxima and minima in the curves of the solvents was pointed out and likewise the magnitude of the absorption coefficients. The molecular absorption coefficients of solutions of varying concentration were measured and plotted against wave-length and also against concentration. It was found, qualitatively, that, in general, the molecular absorption coefficient is not a constant as would be necessary from Beer's law, but varies with the dilution, in some cases increasing and in others decreasing on dilution. The deviations are comparatively small except at certain points in the spectra near a solvent band head, but no quantitative explanation is offered beyond the general hypothesis of solvent complex or solvate formation, which, in fact, would nullify their original assumption that the absorption coefficient was made up of that of the solvent and that of the solute as such. There remains the possibility, however, that Jones was finding the same difficulty as that experienced by the author mentioned previously, namely, that the apparent absorption coefficient, as directly measured by the instrument employed, is not a constant but depends on the thickness used (a point apparently peculiar to the radiomicrometer); the results would not then be comparable between different solvents, even using the same thickness of solution throughout, as was actually the case. Nevertheless, the data collected may be useful and would probably repay the time spent in an attempt to elucidate an explanation. The region examined is an extremely useful one from the point of view of the radiation theory of chemical reaction as will be seen later, and would probably assist in the solution of the mechanism of the action of such salts as catalysts.

So far, we have dealt only with the causes and results of absorption in the near infra-red. Mention has already been made of the residual ray method of Rubens for finding the absorption of bodies in the far infra-red, and a rough outline of the method given. The original papers [2] should be consulted to obtain some idea of the extent and thoroughness of the work. To take but one example, quartz was found to absorb, amongst other positions, at 8.85 μ and 20.75 μ. The question again arises, how are we to account for these positions from the point of view of the constitution of the quartz molecule? The answer may be best given by an example due to Campbell.[3] Assuming the

[1] Hulbert and Hutchinson, *Carnegie Inst. Washington*, No. **260.**

[2] *Inter alia*, Rubens and Aschkinass, *Ann. Physik*, **65**, 241 (1898). Rubens and Wood, *Phil. Mag.*, **21**, 249 (1911).

[3] Campbell, *Modern Electrical Theory*, 2d Ed., pp. 46–48.

validity of the electronic theory of dispersion, it may be shown that the electrons are not the only charged systems in a medium which, under the action of elastic forces, have free periods capable of affecting the refractive index; there are also the atoms and molecules containing these electrons. On displacement of an electron, such systems become positively charged and come under the influence of forces due to the neighboring molecules, possibly causing them to vibrate with periods approximately the same as that of light. Making due allowance for such possible changes, it is found that agreement between experimentally determined infra-red frequencies and those calculated on the above basis is only rendered possible by ascribing to the molecule under consideration a definite constitution. Thus, on the simple basis of the theory, it may be shown that

$$\frac{B_n}{\lambda_n^4} = \frac{N_n e^2}{\pi m_0 c^2},$$

where N_n is the number of electrons of mass m_0 and charge e in unit volume, having a free period corresponding to λ_n, c is the velocity of light in vacuo and B is a constant measurable experimentally for each wave-length $\lambda_1, \lambda_2, \lambda_3 \cdots \lambda_n$. Assuming now that, together with the electrons, a part of the molecule is also capable of vibrations corresponding to λ_n, we must replace N_n by N the number of molecules per unit volume, e by ke where k is an integer and m_0 by Wm where W is the molecular weight of that part of the molecule which is capable of vibrating and m is the mass of the hydrogen atom (taking hydrogen as the basis of atomic weight). Hence,

$$\frac{B_n}{\lambda_n^4} = \frac{Nk^2c^2}{\pi W m c^2}.$$

Rubens found, for quartz, that the values of B_n corresponding to the absorption wave-lengths 8.85 μ and 20.75 μ were

$$B_1 = 4.745 \times 10^{-7} \quad \text{and} \quad B_2 = 5.930 \times 10^{-6}$$

when

$$\lambda_1 = 8.85 \times 10^{-4} \text{ cm.}, \quad \lambda_2 = 20.75 \times 10^{-4} \text{ cm.}$$

Substituting in the above expression we obtain:

$$W = k^2 \times 1.68 \quad \text{and} \quad W = k^2 \times 4.05.$$

If we put $k = 4$ and 2 respectively in these equations, we get $W = 27$ and 16 approximately. However, since the atomic weights of silicon and oxygen are 28 and 16, it is reasonable to infer that the infra-red frequencies corresponding to the wave-lengths observed are due to (*a*) an atom of silicon carrying four electrons and (*b*) an atom of oxygen carrying two electrons. Thus, with the aid of present electronic theories, we are able to ascribe each definite absorption frequency to the vibration of a definite arrangement within the molecule, which is of great assistance in the elucidation of constitution.[1]

[1] See also, Eucken, *Jahrb. f. Rad. u. Elektronik*, **17**, 361 (1920).

Effect of Temperature on Absorption

Coblentz (*loc. cit.*) finds in his investigations of the infra-red absorption spectra that, for a rise of 10 or 15° C., the effect on the absorption is practically negligible, but notices that there may be a slight shift of the head of the band towards the longer wave-lengths. Grantham [1] studying the effect of temperature on the absorption of certain colored glasses, over the range 80–300° C., finds that, as the temperature rises, the absorption decreases slightly in the region of an absorption band and causes a shift of the transmission band towards the longer wave-lengths; the shift is greater on the more refrangible side of the band.

Reinkober [2] arrives at the same conclusions from a study of the selective reflection of ammonium salts in the infra-red, over the temperature range − 175° C. to 120° C. He finds that decreasing the temperature gives an increase in the reflection intensity (which is equivalent to an increase in the absorption) and that the selective bands become sharper and shift towards the shorter wave-lengths. The effect is not very large considering the temperature range, but is sufficiently marked to be determinable accurately.

This definite temperature effect must not be confused with that previously mentioned, where a difference in temperature was giving rise to fictitious readings in the transmission values, although the above true effect would also be entering in as well.

Radiation Theory of Chemical Reaction

The study of infra-red absorption spectra has, of late years, received a definite impetus owing to the recent theories of chemical reaction. The fundamental problem for the chemist today is the determination of the primary cause of reaction. That this is to be identified with the radiational environment and the ability of molecules to absorb energy is the simple basis of the Radiation Hypothesis as suggested by Trautz,[3] Lewis [4] and Perrin.[5] Kruger [6] had shown that such phenomena as solution, solubility, solution pressure and electrolytic dissociation may be explained qualitatively on the basis of radiation, since each could be linked up with the dielectric constant. Trautz, too, had pointed out that even thermal reactions, that is, reactions in which the temperature of the effective radiation is identical with that of the system, may be regarded as ultimately photochemical, namely, brought about by the absorption of radiation, with the distinction that such thermal reactions are due to absorption of infra-red radiation.

The work of Lewis and Perrin was to extend this idea and to make it applicable in a quantitative manner. The definite advance made is due to

[1] *Phys. Rev.*, **16**, 565 (1920).
[2] *Z. Physik*, **3**, 318 (1920).
[3] *Z. anorg. Chem.*, **102**, 81 (1918); **106**, 149 (1919).
[4] *J. Chem. Soc.*, 1914–22. *J. Am. Chem. Soc.*, 1922 et seq.
[5] *Ann. de Phys.*, **11**, 4 (1919).
[6] *Z. Elektrochem.*, **17**, 453 (1911).

the quantization of the radiation which could effect reaction. The theoretical treatment of the theory being more fully dealt with elsewhere, it remains only for us to consider the general bearing which infra-red absorption spectra have on the theory.

The simplest formulation of the radiation theory of ordinary or thermal reactions as developed by Lewis assumes that chemical change is due to a specific frequency of radiation characteristic of the substance involved. Introducing the concept of activation inherent in Marcelin's [1] statistical treatment and combining Marcelin's equation for the critical increment or energy of activation with the radiational equation based on the above assumption, we are led, of necessity, to a relation for thermal reactions which is identical with that of Einstein for photochemical processes. One quantum of energy, of the characteristic frequency ν involved, is necessary to decompose or activate a single molecule. From the numerical values of critical increments (which are obtained directly from measurements of the temperature coefficients of velocity constant), together with the above relation, it is possible to calculate the activating frequency or wave-length. Such calculations show that for the majority of reactions this lies in the short infra-red.

Thus, according to Marcelin and Rice,

$$\frac{d \log k}{dT} = \frac{E}{RT^2},$$

where k is the velocity constant of the reaction, T is the absolute temperature, R is the gas constant, and E is the amount of energy necessary to raise the average internal energy of the molecule to the critical energy, having which the molecule will react.

On integrating the expression we have

$$\log \frac{k_2}{k_1} = \frac{E}{R}(1/T_1 - 1/T_2).$$

Knowing the velocity constant at two temperatures or, what is equivalent, the temperature coefficient of velocity constant, we may calculate the critical increment E. Then, employing the radiation expression, which is identical with Einstein's photochemical law, namely,

$$E = Nh\nu,$$

where N is the Avogadro number, h is Planck's constant and ν is the frequency characteristic of the absorbable radiation, we may find the value of the frequency ν and hence calculate the corresponding wave-length λ. As has been said, for most reactions, this wave-length is found to lie in the short infra-red region, and to confirm the theory most directly there remains to show, first that the reacting substance will absorb radiation at this position, and, secondly, that on absorbing this energy the system will react more rapidly than it would if it were unexposed to such radiation.

[1] *Compt. Rend.*, **158**, 161 (1914). See also Rice, *Brit. Ass. Rep.*, 397 (1915).

The first direct proof that a substance which is undergoing change exhibits a characteristic absorption band the position of which is in quantitative agreement with that calculated on the radiation hypothesis was obtained by the author recently.[1] The reaction studied was the decomposition of triethyl sulphonium bromide in various solvents, the kinetics of which reaction had been previously studied by von Halban.[2] A Hilger infra-red spectrometer, and a radiomicrometer as measuring instrument were used. The absorption spectra of the pure solvent and of a solution of the triethyl sulphonium bromide in the solvent were examined and superimposed. It was found that the curve for the solution exhibited in every case a new band which was not present in the solvent curve. This new band was due to the bromide present and the position was found to agree satisfactorily with that calculated according to the theory. Thus, from the results of von Halban, for the rate of decomposition of the bromide in eight different solvents, the position of absorption was calculated according to the theory and compared with the positions observed. The following table shows the values obtained.

TABLE I

ABSORPTION OF TRIETHYL SULPHONIUM BROMIDE

Solvent	Observed Wave-length in μ	Calculated Wave-length in μ
Nitrobenzene	1.05	1.00
Tetrachloroethane	0.90	0.91
Propyl Alcohol	0.89	0.84
Amyl Alcohol	0.83	0.85
Benzyl Alcohol	0.80	0.78
Acetic Acid	0.93	0.97
Acetone	1.30	0.96
Chloroform	1.00	0.85

The agreement between the calculated and observed positions of absorption is satisfactory in the case of the first six solvents. In the case of acetone, von Halban shows that triethyl sulphonium bromide is ionized in that solvent, whilst it polymerizes in chloroform, yielding velocity constant data which show little or no concordance among themselves and are therefore not strictly amenable to the above calculation. In the latter case, however, one is led to conclude that the polymerized molecule does not decompose as a whole but first depolymerizes before decomposing into ethyl bromide and diethyl sulphide.

Other examples which have not only offered confirmation of the theory but have led to a definite indication of the mechanism of the reaction have been studied.[3] In this case, the temperature coefficient of the velocity of inversion of sucrose as found by Moran suggested on the radiation theory that

[1] Taylor and Lewis, *J. Chem. Soc.*, **121**, 665 (1922).

[2] *Z. physik. Chem.*, **67**, 129 (1909).

[3] Moran and Taylor, *J. Am. Chem. Soc.*, **44**, 2886 (1922).

sucrose should absorb in aqueous solution at 0.815 μ. The position of the band observed at 0.875 μ is in satisfactory agreement when allowance is made for the fact that sucrose in water is possibly present as a tetrahydrate whereas the inversion process is said to proceed from sucrose dihydrate. Further, since an aqueous solution of fructose also absorbs at 0.875 μ whilst a glucose solution does not, the result suggested that the sucrose inversion originates in the fructose portion of the sucrose molecule.

Some work with Garrett was on the hydrolysis and formation of γ-butyrolactone from γ-hydroxybutyric acid. The observed bands in aqueous solution again agreed well with those calculated from the kinetics. Other cases have been studied with similar results and will be found in the original papers in the literature.

That the energy required for reaction may be absorbed not in a single quantum of a certain frequency as required by the first simple statement of the theory, but in terms of several quanta at a correspondingly lower frequency is evident from the experiments of Daniels and Johnston.[1] From their data it is found that the critical increment of nitrogen pentoxide is 24,700 calories and this should correspond to a wave-length 1.16 μ. The authors find, however, that radiation of this wave-length does not decompose nitrogen pentoxide. Hence, the thermal process does not occur through one quantum at this frequency. Daniels and Johnston point out that 1.16 μ corresponds to a frequency exactly five times the most marked band in the infra-red spectrum of nitrogen pentoxide, namely, at $\lambda = 5.81$ μ observed by Warburg and Leithauser;[2] even though the authors do not explicitly connect the two observations, it is evident that the possibility of making up the required energy in terms of five such sub-quanta presents itself. Further, nitrogen pentoxide possesses another band at 3.4 μ which is approximately three times that calculated, in which case three sub-quanta at 3.4 μ would be sufficient to furnish the required energy for the reaction.

A further case investigated by the author is in the formation of dianthracene from anthracene.[3] It was found that thermal polymerization might occur, in solution in phenetol, by means of four quanta at a frequency corresponding to 1.8 μ at which position a solution of anthracene in phenetol does absorb; photopolymerization occurs at 460 $\mu\mu$.

Attempts which have been made so far towards the second confirmation of the theory, namely, to show that radiation of the characteristic frequency is photochemically efficient in accelerating the reaction, have not met with the success which might be expected. The results in the increased hydrolysis of methyl acetate in presence of sunlight as studied by Rideal and Hawkins[4] can be explained on the basis of experimental error alone. The acceleration of the inversion of sucrose, maltose and other sugars under the action of tropical

[1] *J. Am. Chem. Soc.*, **43**, 72 (1921).
[2] *Ann. Physik*, (IV) **28**, 313 (1909).
[3] *J. Am. Chem. Soc.* **46**, 1606 (1924).
[4] *J. Chem. Soc.*, **117**, 1288 (1920).

sunlight as given by N. Dhar [1] has been questioned by Lindemann and Taylor [2] and by H. S. Taylor.[3] Other cases than those of the sugars are also quoted by Dhar.[4] The reaction between oxalic and chromic acids in presence of manganous sulphate and sulphuric acid as catalyst is said to proceed four times as fast when exposed to sunlight as when unexposed. Oxalic acid and potassium permanganate react in presence of the same catalyst with twice the speed when exposed as when unexposed. Similarly sodium formate and iodine have their speed of interaction increased threefold on exposure, whilst potassium oxalate and iodine show a marked increase in reaction velocity when exposed to sunlight. In the latter case Dhar states that the reaction is accelerated by blue, green or violet lights but to a different extent in each case, suggesting that the activating light is not necessarily restricted to one frequency. Perrin, in this regard, has suggested that, in place of one single frequency being active, it might be a series of frequencies acting consecutively and giving rise to the well-known intermediate compounds.

A recent attempt in Lewis's laboratory seems apparently to have given a definite increase in the velocity of inversion of an aqueous solution of sucrose, linear with the time of exposure, to infra-red radiation, which was restricted by water filters to the effective region, namely, 1.0 μ approximately. The fact that the thickness of the illuminated solution is generally confined to a fraction of a millimeter owing to the high absorption coefficient of the solvent suggests that an observed photochemical acceleration in this region may be due to a purely localized heating effect and not to a true photo-effect, if such a distinction can be drawn at all in a region where the solvent itself strongly absorbs. Attention will probably have to be paid to gaseous reactions into which the problem of solvent media does not enter, although the mere existence of photochemical reactions of any kind is an indirect confirmation of the basic principle, namely, that radiation is the means whereby a substance obtains the necessary energy for reaction.

That the existing statement of a radiation theory is the correct one is not a matter to be discussed here, neither are we concerned to what extent the present so-called confirmation of the theory holds; suffice that it has been of interest to see in what way radiation, more particularly of the short wave infra-red region of the spectrum, is of service, or possible service in the production of chemical reaction, and how, that being so, one can attempt to prove or disprove the legitimacy of such ideas.

To the research chemist of today, particularly in the physical branch, there are many widely differing fields for promising investigation. The subject of this chapter forms one of those fields, which, up to the present, has received less attention, perhaps, than any other, the reason probably lying in the

[1] N. Dhar, *Proc. Akad. Vetensk. Amsterdam.*, **14**, 1324 (1916), **23**, 308 (1920); *Z. anorg. allgem. Chem.*, **119**, 177 (1921).

[2] Lindemann and Taylor, *Nature*, **110**, 210 (1921).

[3] H. S. Taylor, *J. Franklin Inst.*, **197**, 15 (1922).

[4] N. Dhar, *J. Chem. Soc.*, **123**, 1856 (1923).

difficulty of the work. It has been the aim of the writer to interest the research student in this branch by placing at his disposal accurate methods for the measurement of infra-red radiation, and by pointing out, though in a somewhat meagre manner, the manifold applications of such measurements to other branches of science. The lack of data generally in this region is of constant trouble to the worker in other fields. More exact data on the infra-red region would well repay the efforts of a number of investigators.

CHAPTER XX

COLLOIDAL CHEMISTRY

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An ideal solution is a mixture of molecules, the properties of which are the sum of the properties of the components when the latter are so measured as to express their proportion of the total number of molecules or integral particles. The above statement contains a generalization or law of solution that has played a major rôle in the development of theoretical chemistry. That solutions consist of a mixture of molecules or ions that are independent of each other must be considered as an ideal condition that is, in reality, hardly ever fulfilled. Deviations occur in practically all solutions. In the first place, attractive forces exist between the various components, and secondly the ultimate particles are not always single molecules or ions. Therefore, real solutions obey the law of mixtures only in special cases, or when one of the components of the solution is present in extremely small proportion.

If the solution contains particles that are larger than single molecules or ions, we have a type of solution that presents problems of interest from many different points of view. Such solutions are called colloidal solutions. As examples we may cite: smoke, fog, gelatine solution, gold sol, finely divided cadmium in solid cadmium chloride. It will be noted that we have not restricted ourselves to the liquid state but have included both the solid and the gaseous states in our definition of a colloidal solution. Such an extension is quite warranted in view of the very general definition of solution that we have adopted.

If the above concept of a colloidal solution is correct, it is evident that great attention should be given to the question of the maximum and minimum size of the aggregate that determines the colloidal state. Unfortunately, it is impossible to distinguish sharply between true solutions, colloidal solutions, and suspensions. Furthermore, it is frequently observed that solutions are encountered that satisfy the criterion of true solution, i.e., the solute comprises single molecules, and yet exhibit many of the properties of colloidal solutions. Such behavior is shown by certain dyes of large molecular weight. For the purpose of rough orientation, a solution that contains a component between 1 $\mu\mu$–200 $\mu\mu$ in diameter may be said to show the properties of a colloidal solution. Such a component is usually termed the disperse phase, while the remainder of the solution is called the dispersion medium. It must not be forgotten that the dispersion medium is more finely divided than is the disperse phase itself, in other words the former phase is subdivided until the molecular

state is reached, while in the case of the disperse phase the subdivision is arrested before the particles consist of single molecules.

We have said that colloidal solutions exhibit properties that differ from those of true solutions. For example, a colloidal solution of sulphur in water presents marked differences in properties from a solution of the same concentration of sulphur in carbon disulphide. The differences are found in certain optical properties such as color, Tyndall phenomenon, etc., in properties that depend upon diffusion, in the colligative properties, and there is also great difference in the stability of the two solutions. Furthermore, the viscosity of colloidal solutions often becomes very great, in fact the entire solution sometimes congeals to a stiff jelly which, in the case of aqueous solutions, is termed a hydrogel.

Many other properties, which may be regarded as corollary to the above, serve to distinguish colloidal from true solutions. An explanation of these differences constitutes the subject matter of theoretical colloidal chemistry, while a systematic compilation of the various colloidal solutions together with a description of properties and methods of preparation may be said to constitute descriptive colloidal chemistry. It is the purpose of the following pages to devote practically our complete attention to a discussion of the theoretical aspects of colloidal chemistry, touching on the descriptive side only insofar as it is necessary to elucidate our argument.

By a theoretical treatment is meant the correlation of as many of the facts of descriptive colloidal chemistry as possible with a few fundamental assumptions. It is very improbable that we can find a satisfactory answer to all of our problems at the present time, for many of the experimental observations are in incomplete form, and furthermore it is quite possible that our fundamental postulates are not correctly stated. For example, great difficulty has long been experienced in accounting for the phenomenon of hysteresis in the case of the adsorption of vapors by certain adsorbents.[1,2] When it was shown that such behavior was immediately connected with the presence of small amounts of permanent gases, the problem acquired an entire change of aspect.[3] von Schroeder's paradox[4] is a similar example of the influence of experimental error on theoretical principles.

The two postulates that serve for the correlation or explanation of colloidal phenomena are: the kinetic theory of matter and the forces of molecular attraction. It will be necessary to treat of these ideas in some detail in the following sections in order that these postulates may be in the proper form, i.e., the kinetic theory must be developed to apply particularly to the movement of large particles, and some satisfactory method of evaluating molecular attraction must be selected.

[1] van Bemmelen, *Z. anorg. Chem.*, **5**, 466 (1894); **13**, 233 (1897); **18**, 14 (1898); **30**, 265 (1902).

[2] J. S. Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

[3] McGavack and Patrick, *J. Am. Chem. Soc.*, **42**, 946 (1920).

[4] v. Schroeder, *Z. physik. Chem.*, **45**, 109 (1903).

Brownian Motion

According to the equipartition of energy, in a system of particles in thermal vibration at constant temperature, each particle possesses the same kinetic energy regardless of its size. This is a most important principle that underlies all the colligative properties of solution, and with its aid one can readily understand the movement of colloidal particles or even particles of microscopic size. It is possible to calculate the velocity of movement of any particle in a given system provided one knows the velocity of *one* of the vibrating particles. For example, if we assume the mean velocity of the water molecule at room temperature to be $150m$/sec., the mean velocity of a particle of 0.4 μ in diameter is found as follows: Let m_1 and m_2 be the molecular weights of the large particle and the water molecule respectively, and c_1 and c_2 be the respective velocities.

$$\tfrac{1}{2}m_1c_1^2 = \tfrac{1}{2}m_2c_2^2,$$
$$c_1 = c_2\sqrt{m_2/m_1},$$
$$\text{and } m_1 = \tfrac{4}{3}\pi(0.2)^3 \times 10^{-12}\delta N = 2.4.10^{10},$$

where δ = density of particle, N = Avogadro's Number;

$$\therefore \quad c_1 = 0.4 \text{ cm./sec.}$$

Actual microscope observations of particles of the above size, however, show a velocity of about 0.0004 cm./sec., i.e., a thousand fold smaller than the theoretical velocity. This discrepancy is not serious when we consider the shortness of time that is necessary to employ in order to observe the true velocity. For particles of the above size, the interval of observation must not exceed 1/1,000,000 of a second. What is actually measured in the above case is the horizontal displacement of the particle, which movement is the result of thousands of tiny zigzag paths.

Naturally with decreasing size of particle the movement increases in velocity and distance, and therefore, in the case of colloidal solutions, the Brownian [1, 2, 3] motion becomes most striking. The discovery of the ultramicroscope [4] brought a great deal of attention to this phenomenon and revived an interest in the facts which in the case of the microscopic observations of the botanist Brown were not sufficiently pronounced to warrant a careful investigation.[5] The thermal vibration of colloidal particles is a most interesting field for the application of the theory of probabilities, in fact the latter theory serves as practically the sole guide in the theoretical development of the subject.

A very convenient method of studying the Brownian motion is that afforded by a determination of the distribution of a system of vibrating particles under the influence of the attraction of gravity. It is clear that the action of gravity tends to bring about a condition where all the particles would be brought to

[1] R. Brown, *Pogg. Ann.*, **14**, 294 (1828).
[2] Gouy, *J. Phys.*, **7**, 561 (1888).
[3] v. Smoluchowski, *Ann. Physik*, (4) **21**, 762 (1906).
[4] Einstein, *Ann. Physik*, (4) **17**, 549 (1905).
[5] v. Smoluchowski, *ibid.*, (4) **21**, 756 (1906).

the bottom of the containing vessel, while the Brownian motion tends to keep the particles distributed throughout the system. An equilibrium is established between these two tendencies that results in an unequal distribution of the particles of the system. This method was first employed by Perrin [1] in the case of coarse emulsions, and his findings constituted an important chapter in the development of the kinetic theory. The quantitative relationships are most clearly brought out by considering the action of gravity in causing a change of density at various levels in a long column of gas. This variation of the pressure with the height of a long column of gas is most readily calculated as follows:

Let P_0 and D_0 represent the pressure and density of a gas at the bottom of the column, while P and D give the corresponding values at some point higher up. Assuming Boyle's law

$$D = \frac{P}{P_0} D_0. \tag{1}$$

Furthermore, the variation of the pressure at the point where the pressure is equal to P with any further increase up the column may be written

$$-dP = gDdx, \tag{2}$$

where g is the gravitational attraction. Substituting for D the above expression (1), there results

$$-dP = \frac{PD_0}{P_0} gdx, \tag{3}$$

whence

$$-\int_{P_0}^{P} \frac{dP}{P} = \frac{D_0}{P_0} g \int_{x=0}^{x=x} dx \tag{4}$$

or

$$ln \frac{P_0}{P} = \frac{D_0}{P_0} gx. \tag{5}$$

Substituting for the gaseous density its value $\frac{P_0 M}{RT}$, where M is the molecular weight, R is the gas constant per mol., T the absolute temperature, we obtain

$$x = \frac{RT}{gM} ln \frac{P_0}{P}. \tag{6}$$

Inasmuch as the pressure of a gas at a constant temperature is a function solely of the number of molecules per unit volume, we may write

$$x = \frac{RT}{gM} ln \frac{n_0}{n}, \tag{7}$$

[1] Perrin, *Compt. rend.*, **146**, 967 (1908); see also "Les Atomes" by Perrin.

where n_0 represents the number of molecules per unit volume at the bottom of the column and n the number at a distance x above the bottom. In the case of colloidal systems the molecular weight of the disperse phase may be expressed as being

$$M = \tfrac{4}{3}\pi r^3(\delta - \delta_n)N, \tag{8}$$

where δ is density of particle, δ_n the density of medium, N is the Avogadro constant. The distribution relationship therefore in the case of colloidal solutions becomes

$$x = \frac{RT}{\tfrac{4}{3}\pi r^3(\delta - \delta_n)Ng} \ln\frac{n_0}{n}. \tag{9}$$

It is therefore clear that systems composed of particles of large diameter should show large differences in concentration, i.e., number of particles per unit volume, with relatively small distances from the bottom of the column. For example, a colloidal gold solution made up of particles 10 $\mu\mu$ in diameter at a distance 10 cm. from the bottom should contain only $\frac{1}{10}$th the number of particles per unit volume that are present in the bottom layer. However, no such differences in concentration are ever observed in the case of colloidal solutions, because of the slow rate of settling of the particles, it being calculable by Stokes' law [1] that gold particles of the above size would require seven years to settle a distance of 10 cm. This fact means that it is practically impossible to obtain a colloidal system of macroscopic dimensions in equilibrium with gravity.

Inasmuch as one of the distinguishing characteristics of colloidal solutions is their small diffusion coefficient, it becomes important to find the quantitative relationship between the rate of diffusion and the kinetic vibration of the particles. It is easy to see in a qualitative sense that the thermal agitation is the mechanism by means of which molecules or particles are transported from one portion of a system to another. It is also readily apparent that the rate of transportation or diffusion should increase with the faster moving particles. The quantitative relation was first worked out by Einstein [2] and depends upon the following considerations:

It is first necessary to state that the Brownian motion of a colloidal particle as observed under the microscope or ultramicroscope does not of course measure the actual velocity of the moving particle. As was shown in the introduction, the time of observation is much too long to permit the observation of the actual motion. One of the early objections to attributing the Brownian motion to the kinetic bombardment of the neighboring molecules was that the collisions

[1] Stokes' Law states that,

$$u = \frac{2}{9}\frac{r^2(d - d_0)g}{\eta},$$

where u is the velocity of the falling particle, r the radius, d the density, d_0 and η the density and viscosity of the medium through which the particle falls under the acceleration of gravity g.

[2] Einstein, *Z. Elektrochem.*, **14**, 235 (1908).

on all sides would be equal in number and therefore leave the large particle with zero resultant motion. This of course is true in the case of very large particles, but it can be shown that, as the particle diminishes in size, the probability of the collisions being equal in all directions becomes smaller and smaller.

The motion of a colloidal particle is therefore entirely chaotic in its character, there being no tendency to move in any particular direction. This last statement is true of each individual particle, but it is equally true that, if any portion of the colloidal system is devoid of its quota of vibrating units, there will be a movement of the particles in that direction so as to equalize the concentration throughout the entire system.

If the distance traveled by a colloidal particle be observed under the ultramicroscope at equal intervals of time, it will be observed that the distances are by no means equal. It is to be remembered that the motion of the particle may equally well take place in a plane parallel to the direction of vision, therefore the motion as seen constitutes only the horizontal displacement. These horizontal displacements of colloidal particles can be directly observed over any period of time, and furnish a most important means of experimentally studying the kinetic theory of matter. It may be said that great theoretical progress has been made along these lines; in fact, the mathematical treatment [1] may be said to constitute a new chapter in applied mathematics.

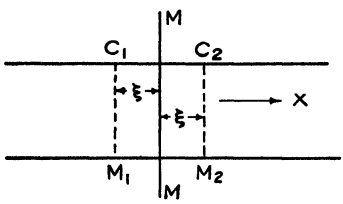


FIG. 1

While it is true that the horizontal displacement of a colloidal particle is not uniform, it is possible to evaluate the so-called mean horizontal displacement by use of the Maxwell distribution law. This mean displacement ξ must therefore be regarded as a quantity of the utmost theoretical significance. Its relation to diffusion may be shown as follows:

Consider the diffusion across the plane M. It is evident that, in order that a particle may pass M, it must be at a distance not greater than ξ from M. Furthermore, it is clear that, in the event of uniform concentration throughout the system, there would be no net change in either direction, i.e., the probabilities would be equally great for the same movement from either side. If, on the other hand, the concentration of particles in the plane M_1 is equal to c_1 and in plane M_2 is equal to c_2, then the diffusion to the right is proportional to $\frac{1}{2}\xi c_1$ and to the left to $\frac{1}{2}\xi c_2$. The factor $\frac{1}{2}$ indicates that the chances are equal for the particle to move either to the left or right. Therefore, the net effect or the diffusion is proportional to

$$\tfrac{1}{2}\xi(c_1 - c_2). \qquad (10)$$

Assuming that ξ was measured at short intervals of time and is, therefore, a

[1] v. Smoluchowski, *Boltzmann-Festschrift*, 1904. *Physik. Z.*, **13**, 1069 (1912); **16**, 321 (1915); **17**, 557 (1916).

small distance, we may write

$$\frac{c_2 - c_1}{\xi} = \frac{dc}{dx}, \tag{11}$$

where x is the distance along the line of diffusion. Therefore,

$$c_1 - c_2 = -\xi \frac{dc}{dx}, \tag{12}$$

which when substituted in the equation (10) gives

$$-\frac{1}{2}\xi^2 \frac{dc}{dx}$$

as the number of particles passing through the plane M. In unit time this would become

$$-\frac{1}{2}\frac{\xi^2}{t}\frac{dc}{dx}. \tag{13}$$

By definition, the coefficient of diffusion (D) is the number of particles passing a given plane in unit time when the concentration gradient, i.e., dc/dx, is equal to unity. We may therefore write

$$D = \frac{1}{2}\frac{\xi^2}{t}. \tag{14}$$

This relationship clearly indicates the intimate connection between diffusion and the kinetic motion of the molecules or particles. Furthermore, as the coefficient of diffusion at constant temperature is a constant with any given solution, it follows that

$$\frac{\xi^2}{t} = K, \tag{15}$$

or, that the mean horizontal displacement is proportional to the square root of the time of observation.

Einstein and Smoluchowski have also carried through a mathematical analysis by considering the Brownian motion of a particle as the source of its osmotic pressure and were led to the following conclusion:

The velocity with which a single particle moves may be written

$$u = \frac{k}{F}, \tag{a}$$

where u is the velocity, k the force causing the motion, and F the frictional resistance. In a similar manner we may write the velocity of diffusion of all the particles of a solution of concentration (c) across a given plane

$$u = \frac{1}{cN}\frac{K}{F}, \tag{b}$$

K now being the force acting on all the particles, and N Avogadro's number. K is furthermore equal to the osmotic pressure gradient, i.e.,

$$K = -\frac{dP}{dx},$$

inasmuch as $P = RTc$ (as a first approximation),

$$K = -RT\frac{dc}{dx}; \tag{c}$$

substituting (*c*) in (*b*),

$$uc = -\frac{RT}{NF}\frac{dc}{dx}. \tag{d}$$

Making use of the law of frictional resistance that applies to a moving particle of radius (r) in a medium of viscosity (η),

$$F = 6\pi\eta r; \tag{e}$$

substituting (*e*) in (*d*), we have

$$uc = -\frac{RT}{6\pi N\eta r}\frac{dc}{dx}. \tag{f}$$

uc is the amount of material that has diffused across the imaginary boundary in unit time, and this quantity under conditions of unit concentration gradient, i.e., $\frac{dc}{dx} = 1$, is nothing but the diffusion coefficient D.

Therefore,

$$D = \frac{RT}{6\pi N\eta r}, \tag{16}$$

an equation that allows the calculation of Avogadro's number (N) from the measurements of the mean horizontal displacement of a colloidal solution composed of particles of radius r. The above equation may also be written in the form

$$\frac{\xi^2}{t} = \frac{RT}{3\pi N\eta r}, \tag{17}$$

which allows the calculation of size of particles from diffusion measurements, and also affords a convenient method of evaluating Avogadro's number.

Molecular Attraction

It is proposed to develop the theory of colloids around the postulates of molecular attraction and molecular kinetic motion. In the preceding section the kinetic theory was developed as applying particularly to particles of colloidal dimensions. It is first necessary to understand what is meant by the term molecular attraction.

The attractive forces between atoms that operate to form molecules or compounds are well known. Such forces are usually of great magnitude, their existence being manifested by the appearance of heat, light, electrical energy, etc. The subject of thermodynamics affords us a method of successful inquiry into the quantitative investigation of such chemical forces. Another characteristic of these forces between atoms is summarized in the laws of definite and multiple proportions, i.e., with each atom there is associated the ability to combine to a fixed extent with other atoms.

It soon became evident to physicists and chemists that there also exists an attractive force between molecules in the gaseous state and in solutions. In other words, we can no longer consider a gas or a solution as a simple mixture of molecules absolutely independent of each other. This force between molecules differs not so much in intensity from the chemical force between atoms as it does in its non-adherence to the laws of definite or multiple proportion. van der Waals applied this idea in his well-known equation of state. The Joule-Thomson heat effect also affords a most striking and direct manifestation of these molecular forces.

Unfortunately, these two means of attack apply practically only to the gaseous state while most of our interest centers in the liquid state. It is evident from van der Waals' equation that the molecular attraction must increase enormously as we pass from the gaseous to the liquid state. Expressing the van der Waals equation in the form

$$P = \underset{\text{(thermal pressure)}}{\frac{RT}{V-b}} - \underset{\text{(molecular attraction)}}{\frac{a}{V^2}}, \tag{18}$$

we see at a glance that when V represents the molal volume of liquid then the second term on the right, the "negative pressure," must become very great. This pressure is called the internal pressure (Binnendruck). Unfortunately, we have no direct method of evaluating this most important quantity, but must content ourselves with relative changes and approximate absolute values. It is certain that the accurate measurement of this quantity would lead to important advances in the theory of the liquid state.

The internal pressure has been shown to be related to the latent heat of vaporization, surface tension, and the compressibility of liquids. This is but another way of saying that all of the above properties, including the internal pressure, are manifestations of the same phenomenon, i.e., molecular attraction. It is customary to coin a name to include a closely related group of properties, and accordingly those properties of solutions or liquids that are in causal relation to the forces of molecular attraction are termed lyotropic. We have thus two great groups of properties of solutions, the colligative, and the lyotropic.

Surface Tension: It would be possible to select any of the lyotropic properties as a basis for the estimation of the molecular attraction, but none permit

of such easy measurement as does the surface tension. It may be said that no property of matter permits of so many and diversified methods of measurement.[1] Surface tension expresses the free energy that is necessary to form 1 cm.^{2} of surface, i.e., it measures the work that is done in bringing the molecules from the interior to the surface of a liquid. Solids of course possess a surface tension but, as yet, no direct means has been devised for measuring the same.

The surface tension of water is 72 ergs/cm.^{2} at room temperature, but the total energy involved in the formation of 1 cm.^{2} of water surface is 119 ergs. In other words, (119 − 72) or 47 ergs are latent and appear in the form of heat during the change of state. The above facts which may be easily correlated with the aid of thermodynamics take the following algebraic form (cf. Gibbs-Helmholz equation, page 65):

$$H = \sigma\omega - T\omega\frac{\delta\sigma}{\delta T}, \tag{19}$$

where σ = the surface tension per cm.^{2}, and H the total energy involved in the formation of ω cm.^{2} of surface at the temperature T.

We have spoken of the surface tension of water, but a moment's reflection will reveal a certain ambiguity in this expression, for it is evident that the surface of a liquid must be in contact with some other phase of matter and any variation in this latter phase will influence the value of the surface tension at the boundary. Ordinarily, a liquid is in contact with its saturated vapor, for, even when the liquid is in contact with air, it may be safely assumed that there is, next to the surface of the liquid, a layer of saturated vapor. In case the liquid is in contact with another liquid, an increase in the surface between the two liquids involves bringing both kinds of molecules from the interior of the two liquids. Naturally, such an operation requires an expenditure of work that is quite different in magnitude from that required to increase the surface of one of the liquids against its saturated vapor. The free energy involved in the increase of 1 cm.^{2} of surface between two liquids is called the interfacial tension.

The force of molecular attraction varies with the temperature and, accordingly, the surface tension changes with the temperature. In the case of liquid-saturated vapor interfaces the tension always decreases with increasing temperature, becoming zero a few degrees below the critical temperature, while the interfacial tension may possess a negative or positive temperature coefficient depending upon the critical solution temperature of the system. The temperature-surface tension relationships are summarized in the following equation:

$$\sigma_1 = \sigma_0[1 - \gamma(t_1 - t_c)], \tag{20}$$

which shows σ varying as a linear function of the temperature. This equation of Eötvös,[2] Ramsay and Shields [3] expresses the fact already mentioned that

[1] Freundlich, Kapillarchemie (1922), pages 17–38.

[2] Eötvös, *Wied. Ann.*, **27**, 448 (1886).

[3] Ramsay and Shields, *Z. physik. Chem.*, **12**, 433 (1893).

TABLE I

SURFACE TENSION OF LIQUIDS

Liquid	Temp.	σ
Hydrogen [1]	− 252	2
Nitrogen [2]	− 195.9	8.3
Oxygen [3]	− 182.7	13
Carbon Dioxide [4]	+ 15.2	1.8
Ammonia [5]	− 29	41.8
Sulphur Dioxide [6]	− 25	33.5
Silver [7]	+ 1060	750
Mercury (in vacuum) [8, 9]	+ 15	436
Benzene [10]	+ 20	28.8
Ethyl Alcohol [11]	20	22.0
Ethyl Ether [12]	20	16.5
Glycerine [13]	18	64.5
Anilin [14]	20	43.8

TABLE II

INTERFACIAL TENSION BETWEEN TWO LIQUIDS

	σ
Mercury—Water (20°)	374.8
" —Ethyl Alcohol (20°)	364.3
" —Benzene (20°)	362.8
Water—Benzene (20°)	32.6
" —Isobutyl Alcohol (20°)	1.76
" —Isoamyl Alcohol (20°)	4.42
" —Ethyl Ether (20°)	9.69
" —Chloroform (20°)	27.7
" —Carbon Tetrachloride (22°)	43.4
Methyl Alcohol—Carbon Disulphide (18°)	0.82

the free surface energy vanishes in the neighborhood of the critical temperature. The above investigators also showed that the free surface energy of one mole of a liquid was a constant quantity provided the measurement was made at a corresponding temperature. The molal surface is the minimum surface presented by one mole, i.e., when the latter is in the form of a sphere. If ω is the surface of a sphere of volume V, then

$$\omega = 4\pi r^2,$$
$$V = \tfrac{4}{3}\pi r^3;$$
$$\therefore \quad \omega = kV^{2/3},$$

[1] Dewar, *Proc. Roy. Soc.*, **68**, 360 (1901).
[2, 3] Baly and Donnan, *J. Chem. Soc.*, **81**, 97 (1902).
[4] Verschaffelt, *Ver. K. Akad. Wetens. Amst.*, **4**, 74 (1895).
[5, 6] Grummach, *Drud. Ann.*, **4**, 367 (1901).
[7] Gradenwitz, *Wied. Ann.*, **67**, 467 (1899).
[8] Stockle, *ibid.*, **66**, 499 (1898).
[9, 14] Volkmann, *ibid.*, **56**, 457 (1895).
[10, 11, 12] Ramsay and Shields, *Z. physik. Chem.*, **12**, 433 (1893).
[13] Cantor, *Wied. Ann.*, **47**, 399 (1892).

and since the molal volume $= M/\delta$, the Eötvös equation is written

$$\sigma(M/\delta)^{2/3} = k(\theta - T - \tau). \tag{21}$$

It is thus seen that the free molal surface energy decreases with increasing temperature, becoming equal to zero τ degrees (about 6) below the critical temperature (θ).

The total molal surface energy,

$$(\sigma - Td\sigma/dT)(M/\delta)^{2/3},$$

on the other hand, may be shown to be independent of the temperature as follows:

Let

$$E = \sigma - Td\sigma/dT = \sigma - q.$$

Then

$$dE/dT = d(\sigma - q)/dT = -Td^2\sigma/dT^2.$$

Inasmuch as σ is a linear function of the temperature

$$d^2\sigma/dT^2 = 0, \qquad \therefore\ dE/dT = 0. \tag{22}$$

Should the total surface energy measure the force of molecular attraction, it would necessarily follow that this latter force was also independent of the temperature. It may be of some interest to note that such a conclusion has been reached in other connections. (It is to be understood that the constancy of the total surface energy does not hold for all temperatures, for it is known that the surface tension-temperature curve departs from its linear course in the neighborhood of the critical temperature; furthermore, at extremely low temperatures the Nernst heat theorem would require a similar departure.) It may therefore be well asked why the free and not the total surface energy is so often used in dealing with lyotropic properties. The answer to such a question is one of vital importance.

Our primary interest, from a theoretical standpoint, is to explain the apparent stability of colloidal systems. The kinetic movement or thermal vibration tends to produce a system in a state of greatest subdivision, while the attractive force between the molecules acts in the opposite manner, tending to the formation of matter in the massive state. At the critical temperature all substances pass into the state of molecular dispersion, and we therefore say that the attraction between the molecules becomes inappreciable. This does not necessarily mean that the molecular attraction has been diminished in extent, for the above effect may be entirely due to the increase in kinetic energy of the particles. It is evident that the difference between these two effects is the determining factor. Inasmuch as molecular dispersion becomes greater at higher temperatures, it is obvious that the free surface energy gives a better measure of the tendency of matter to remain in the massive condition than does the total surface energy which does not change with the temperature.

It is therefore evident that there is a continual struggle between the forces that tend to disperse and those that tend to condense matter. In the case of ordinary macroscopic systems the equilibrium between these two forces is determined by the ordinary vapor pressures or solubilities of substances. We must now ask the question as to the effect of the size of particle on the magnitude of these latter quantities. Does a small drop of water possess the normal vapor pressure of water, or is a tiny crystal of barium sulphate as soluble as a large crystal? The answer to these questions only increases our difficulty in explaining the stability of colloidal systems, for it is found that the smaller the particle (provided the curvature is convex) the greater the vapor pressure or solubility. At any rate, it is evident that colloidal systems can only exist with systems of low solubility or vapor pressure.

The above question may be approached in a variety of ways, but, as in most other problems, the quantitative relationships are only to be obtained by a study of the energy changes involved. In other words, we are unable at the present time to deal quantitatively with the problem from the standpoint of a collection of particles in thermal agitation between which there exists an attractive force. However, the above problem may be advantageously studied qualitatively from the latter standpoint. Consider a liquid in the three following forms:

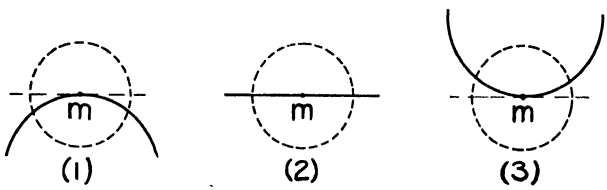


FIG. 2

Let us focus our attention upon a single molecule (m), which is subject to an attractive force exerted upon it by all the molecules within the molecular sphere of action (dotted circle). It can be seen that the attractive force acting upon the molecule is greatest in (3) and smallest in (1), with case (2) intermediate. Since the kinetic energy of the three systems is the same (constant temperature), it follows that a molecule may more easily escape from a liquid surface as in (1) than from any of the other surfaces. Furthermore, inasmuch as the molecular sphere of attraction is known to be small, we may safely reason that the radius of curvature in both cases 1 and 3 must be very small in order to produce a change in vapor pressure from that exhibited by a plane surface of liquid (case 2). As a matter of fact the radius of curvature must be of the order of at least 1 μ (0.001 mm.) before any difference can be detected.

The quantitative relationship is given as follows: Consider two drops of radii r_1 and r_2 having vapor pressures p_1 and p_2. Take a small amount of

liquid dm from r_1 and carry it to r_2, thereby decreasing the surface of the first drop and increasing that of the second. Next distil the same amount dm from the large drop back to the small one. The laws of thermodynamics tell us that the energy change in the above cycle must be equal to zero, and it therefore follows that the work of distillation must be equal and opposite in sign to the surface work.

$$\text{distillation work} = \frac{RT}{M} ln \frac{p_2}{p_1} dm,$$

$$\text{surface work} = \sigma(d\omega_1 - d\omega_2),$$

$$d\omega_1 = \delta\omega_1/\delta m_1 \cdot dm, \qquad d\omega_2 = \delta\omega_2/\delta m_2 \cdot dm,$$

$$\omega = 4\pi r^2, \qquad m = \tfrac{4}{3}\pi r^3 \delta,$$

$$d\omega/dr = 8\pi r, \qquad dm/dr = 4\pi\delta r^2;$$

$$\therefore \quad d\omega = 2dm/r\delta;$$

$$\therefore \quad \frac{RT}{M} ln p_1/p_2 = 2\sigma/\delta(1/r_1 - 1/r_2). \tag{23}$$

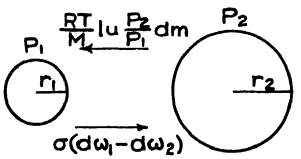


FIG. 3

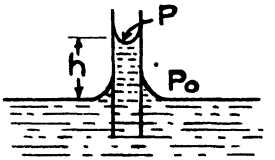


FIG. 4

If $r_1 < r_2$, then $p_1 > p_2$, i.e., the smaller drop exhibits the greater vapor pressure. If r_2 is infinitely great, a plane liquid surface is implied; therefore p_2 represents the ordinary vapor pressure of the liquid at the temperature T. The above equation then reads

$$ln \frac{P}{P_0} = \frac{2\sigma M}{R \times T \times \delta \times r}. \tag{24}$$

If the curvature of the surface of a liquid is concave outwards, it follows from the kinetic-attraction point of view that the escaping tendency must decrease. The above diagram, Fig. 4, will aid in the understanding of the above effect:

P must be less than P_0, for otherwise there would be a condensation of vapor at the level P_0 since the vapor at the point is under a pressure greater than that at P by an amount equal to the weight of the column of vapor (h). In the case of very small tubes, the distance (h) becomes great and therefore the variation of the density of the vapor with the height must be taken into

consideration. By means of a cycle similar to that used in dealing with the vapor pressure at convex surfaces it can be shown that

$$lnP_0/P = \frac{2\sigma M}{RT\delta r}. \tag{25}$$

Both in this and in the preceding equation we have assumed that the vapor obeyed the simple gas law, and that, furthermore, the density of the liquid suffered no change.

A similar set of equations may be obtained showing the influence of surface energy on the solubility of substances—convex curvature exhibiting an increase and concave curvature a decrease in solubility. In this case the interfacial tension is employed instead of the surface tension. The miscibility of two substances in all proportions is an indication that the interfacial tension is zero. Negative surface tensions have been postulated [1] to explain the phenomenon of solution. Such a procedure is equivalent to ignoring the disintegrating influence of the thermal vibration of the molecules and placing the entire effect on the molecular attractive force. Furthermore, as no one has ever measured a negative surface tension, the value of an explanation of solubility from such a standpoint is negligible.

Surface Tension of Solutions: The surface tension of solutions has been the subject of a great many investigations, but the salient facts may be told in a few words. If a solute be added to a solvent, there is every reason to expect a change of the attractive force between the molecules, for this force varies with each molecular species. In other words, the addition of the solute influences the amount of work necessary to increase the surface of the liquid. If the surface tension of a solvent be decreased by the addition of the solute, an obvious interpretation is that the attractive force between the molecules of the solute and those of the solvent is less than the corresponding force between mutual solvent molecules. That is to say, less work is required to bring the solute molecules to the surface than is expended in increasing the surface by means of solvent molecules. Solutes that exhibit such an effect are termed active substances, while those that raise the surface tension of a solvent are called inactive. The well-known Gibb's theory of adsorption is founded upon the above phenomena.

The surface tension of solutions of active substances always exhibits the following characteristic course, the greatest lowering of the surface tension occurs at low concentrations. The data of Tables III and IV are reproduced in Fig. 5. Additional data are plotted in Fig. 6.

It is an illuminating fact that there remains to be found a theoretical formula that satisfactorily expresses the above curves. Freundlich proposes [2] the following empirical formula which approximately gives the relation between the relative surface tension lowering and the concentration:

$$\Delta = \frac{\sigma_0 - \sigma}{\sigma_0} = kc^{1/n}. \tag{26}$$

[1] Tolman, *J. Am. Chem. Soc.*, **35**, 317 (1913).

[2] Freundlich, Kapillarchemie, p. 90 (1922).

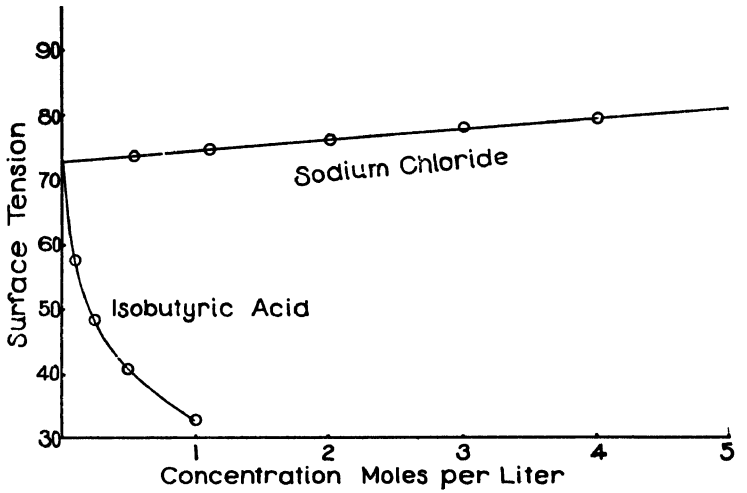


FIG. 5

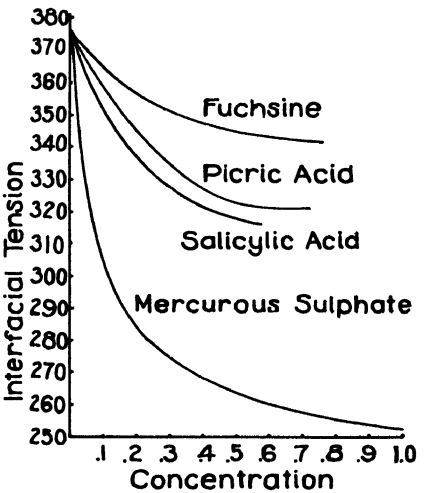


FIG. 6

TABLE III

SURFACE TENSION OF NaCl SOLUTIONS, 18°

C. mole/liter	σ	C. mole/liter	σ
0.000	73.00	1.11	74.77
0.020	73.04	2.06	76.34
0.121	73.20	3.04	78.42
0.290	73.44	4.00	79.86
0.544	73.81	5.43	82.87
0.713	74.19		

TABLE IV

SURFACE TENSION OF ISOBUTYRIC ACID SOLUTIONS, 18°

C. mole/liter	σ	C. mole/liter	σ
0.00	73.0	0.1000	57.7
0.0187	68.6	0.250	48.3
0.0250	67.3	0.500	40.7
0.0500	63.3	1.000	32.6

In order to test the validity of this formula it is sufficient to plot log Δ against log c—a straight line resulting in case the equation accurately reproduces the facts. As may be seen from the following logarithmic curve, there is a perceptible departure from the straight line requirement, thus proving the approximate nature of the formula.

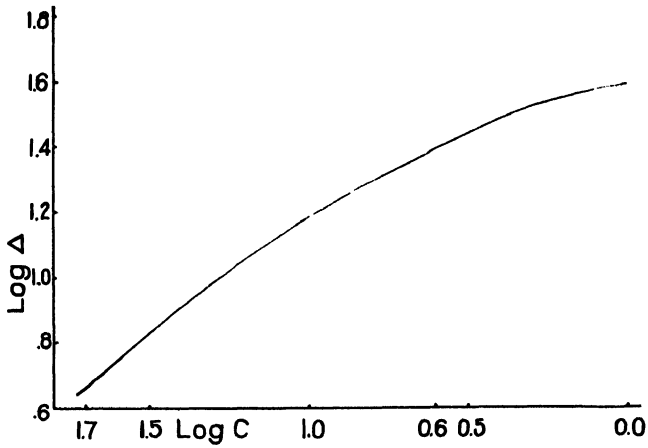


FIG. 7

Szyszkowski proposes [2] the following empirical equation that possesses the merit of at least more closely expressing the course of the surface tension lowering than does the Freundlich equation:

$$\Delta = \beta ln(c/k + 1),$$

β and k being arbitrary constants, the former showing only slight variations from substance to substance while k is a characteristic quantity that has been advantageously taken as a measure of surface tension activity of various solutes.

When $k = c$,

$$\Delta = \beta ln2;$$

using the average value of β, the above lowering equals 0.1387, i.e., k equals the concentration (c) that produces a surface tension lowering of about 14 per

[2] Szyszkowski, *Z. physik. Chem.*, **64**, 385 (1908).

cent. The reciprocal of $k(1/k = C)$ will therefore increase as the activity of the solute increases. It has been found that as the number of carbon atoms in an aliphatic homologous series increases there is a corresponding increase in the surface tension activity. This generalization is known as Traube's Rule.[1]

TABLE V

SURFACE ACTIVITY OF AQUEOUS SOLUTIONS OF FATTY ACIDS

	C	C_{n+1}/C_n
Formic Acid	0.73	
Acetic Acid	2.84	3.9
Propionic Acid	8.93	3.1
n. Butyric Acid	19.6	2.2
n. Valeric Acid	68.5	3.5
n. Capronic Acid	233	3.4
n. Heptylic Acid	555	2.4
n. Octylic Acid	2222	4.0
n. Nonylic Acid	7144	3.2

It is an interesting fact to notice that each succeeding member of the series shows an activity constant (C) that is approximately threefold the value of the preceding member of the series. As the molecular weight increases, the work necessary to bring the substance to the surface of its aqueous solution decreases. From a qualitative point of view this statement teaches us very little, for it is a matter of common knowledge that the solubility in water decreases as we ascend in an aliphatic series.

Langmuir [2] has emphasized the quantitative side of this question and sees in the fact that each successive member of the series requires three times the work to remove it from the surface to the solution (thus reversing the usual point of view) evidence to prove that there is an orientation of the molecules at the surface. Both Langmuir and Harkins [3] have been very diligent in searching for evidence to support this idea, and they have uncovered many striking experimental facts that may be interpreted as showing that the molecules are arranged in a definite manner at the surface. While it is true that it is possible to correlate a great number of facts by means of the idea of a static orientated liquid surface made up of molecules shaped as indicated by the structural formulæ of organic chemistry, it is a matter open to some doubt as to how far this idea should be pressed. This note of conservatism is sounded here with the sole purpose of checking hasty speculation. The great complexity of the problem cannot be too often emphasized when the treatment is from the molecular-kinetic point of view, and the investigator must accept each working postulate with the greatest of caution.

[1] J. Traube, *Lieb. Ann.*, **265**, 27 (1891).

[2] Langmuir, *J. Am. Chem. Soc.*, **39**, 1883 (1917).

[3] Harkins, Davies, Clark, *J. Am. Chem. Soc.*, **39**, 1848 (1917).

Electrokinetic Phenomena

Having discussed the forces of molecular attraction and the thermal agitation of the molecules, it becomes necessary to consider certain electrical phenomena occurring at interfaces that owe their existence to these two general tendencies. It is evident that at the interface between two phases there will exist a distribution of the molecules composing the two phases that differs from that existing in the interior of either phase. This difference arises from the fact that the force of molecular attraction varies in different substances. Any disturbance of this equilibrium arrangement of the molecules at an interface must be accompanied by the exertion of a compensating expenditure of energy.

If the disturbance at the interface takes place by the transportation of matter from one phase to the other, i.e., at right angles to the interface, then the energy requirements are expressed in the ordinary laws of electrochemistry. On the other hand, if the molecular arrangement at the interface is disturbed by a force parallel to the interface, then we are dealing with phenomena that are termed electrokinetic. Perhaps this distinction may be best made clear by the schematic drawings in Fig. 8.

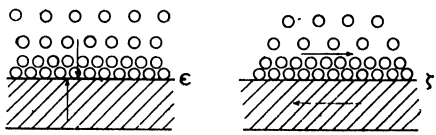


Fig. 8

The transfer of matter from the one phase to the other as indicated on the left is governed by Faraday's law and the laws of electromotive force (ϵ). If, on the contrary, a displacement of the two phases takes place as illustrated on the right the motion is opposed by an electrical force differing markedly from ϵ. The electromotive force in this case, as may be expected, is generally much smaller than ϵ and is designated as the electrokinetic potential or as (ζ). Such a potential at the interface between two phases may be regarded as the causal factor in the phenomena of endosmose, cataphoresis, streaming potential, and the electrical currents produced by falling particles.

In the case of electrical endosmose the movement of a liquid in reference to fixed solid is brought about by the application of an external electromotive force. In cataphoresis the solid particle is moved through the fixed liquid by the same agency. In the streaming potential experiments an electrical current or a difference of potential is shown to be set up by forcing a liquid through a tube. This experiment is nothing but the reverse of the electro-endosmose. It can also be experimentally demonstrated that electric currents are produced by the passage of particles through a liquid or gaseous medium. All the above phenomena are closely related and in fact can be directly connected with the potential existing at the interface between the two phases in question. This potential is quite different in value from the ordinary electromotive force considered in electrochemistry, although it is entirely possible that both are due to the same cause, the difference in magnitude being explained by the fact that, in one case, matter is transported from one phase to the other

while in the other case only a drifting or a displacement of the two phases with respect to each other is brought about.

The exact origin of the electrical charge, with its accompanying difference of potential at an interface, has been the subject of much study and speculation.[1] The most prevalent view is that proposed by Helmholtz,[2] namely, that the charge is the result of a condenser effect with layers of oppositely charged ions forming the condenser or double layer. In order to account for the difference between ϵ and ζ, it becomes necessary to assume two such layers. The double layer next to the condensed phase is very thin, with one of the layers residing in the solid wall itself. This double layer is the seat of most of the potential difference ϵ. The other double layer, sometimes termed the diffusion layer, is much thicker and consists of a fixed and a movable layer of liquid. This double layer is the seat of the potential difference ζ. These two double layers are superimposed upon each other and ordinarily are additive in their effects, ϵ being a measure of the potential due to the two.

The relations between ζ and the movements produced in an electrical field or the reverse phenomenon of an electrical current being produced by the relative motion of one phase with respect to another have been quantitatively evaluated by Helmholtz:[3]

It can readily be shown that the frictional force opposing the motion of a volume of liquid V through a tube of radius r is given by the following:

$$\frac{\eta V}{\pi r^2 \delta}, \tag{27}$$

where η equals the viscosity of the liquid and δ the thickness of the double layer, i.e., the fixed and movable layers of liquid.

The electrical force tending to move the liquid is equal to

$$eH,$$

where e is the charge of the double layer and H the external potential gradient. A condenser of charge e and distance between the layers of δ would show a difference of potential

$$\zeta = \frac{4\pi\delta e}{D}, \tag{28}$$

where D is the dielectric constant of the liquid. The volume of liquid transported is therefore given by a suitable combination of the above as

$$V = \frac{r^2 \zeta E D}{4\eta l}. \tag{29}$$

where E is the externally applied potential and l is the distance between electrodes, i.e., $E/l = H$. Usually the experiments are conducted with a porous

[1] Wiedemann, *Z. physik. Chem.*, **79**, 385 (1912).
[2] Helmholtz, *Wied. Ann.*, **7**, 337 (1879).
[3] *Loc. cit.*

plate instead of a single tube, which fact results in the cross section of the space through which the liquid passes being unknown. The relationship then becomes

$$V = \frac{q\zeta ED}{4\pi\eta l}, \tag{30}$$

q being the unknown cross section. In order to eliminate the cross section from equation (30), the latter is written in terms of the current flowing between the external electrodes instead of in terms of the potential gradient. As $E = RI$, and $1/R = \overline{L}q/l$, where $\overline{L}$ is the specific conductivity, it follows that

$$V = \frac{\zeta ID}{4\pi\eta\overline{L}}. \tag{31}$$

This formula enables one to calculate ζ from measurements of electrical endosmose.

By a similar analysis it can be shown that the velocity with which a charged particle moves through a liquid in an electric field is equal to

$$u = \frac{\zeta ED}{4\pi\eta l}. \tag{32}$$

It therefore follows that ζ may be evaluated from cataphoresis experiments.

Or again, the potential difference observed at the ends of a tube through which a liquid is forced is given by the following relationship:

$$E' = \frac{P\zeta D}{4\pi\eta\overline{L}}, \tag{33}$$

where all the symbols have the usual significance and P denotes the pressure under which the liquid is forced through the tube.

A comparison of the streaming potential and endosmose formulæ will reveal the fact that

$$V/I = E'/P. \tag{34}$$

This relationship allows a convenient method of testing the validity of the above formulæ. Such a test can of course also be made by determining ζ at the same boundary by endosmose, cataphoresis, and streaming potential methods. However, the former method allows one to conclude the general correctness of the existing formulæ as Table VI shows.

The electrokinetic methods afford a convenient means of studying the influence of dissolved matter upon the potential difference of the diffusion double layer. The potential ζ is found to vary greatly with the nature and concentration of the dissolved matter, as well as with the nature of the material of the wall. Most solids are negatively charged against water; oxides, carbonates, and halides are exceptions inasmuch as they carry a positive charge under similar conditions. The above statements are only true in a limited

TABLE VI

COMPARISON OF ELECTRICAL ENDOSMOSE AND STREAMING POTENTIAL

Solution	V/I	E'/P
0.0174 mol. $ZnSO_4$	0.360	0.352
0.0261 " "	0.382	0.379
0.0348 " "	0.346	0.344
0.0195 " $CdSO_4$	0.582	0.588
0.0390 " "	0.116	0.115
0.0400 " $CuSO_4$	0.385	0.385
0.0800 " "	0.233	0.237

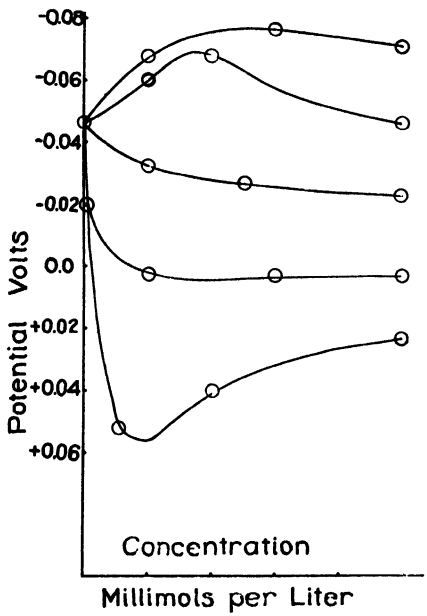


FIG. 9. ζ from cataphoresis experiments. The curves in descending order refer to the influence of $K_4Fe(CN)_6$, KCl, $BaCl_2$, $AlCl_3$ and $ThCl_4$.

sense, as it is possible to change the sign of the charge in most cases by the addition of extremely small quantities of certain active electrolytes to the water.

The relation between ζ and concentration of electrolytes is complicated and may best be summarized by means of a series of experimental curves. The following graphs express the value of ζ obtained from cataphoresis experiments plotted against the concentration of the electrolyte solution. The disperse phase in all cases consists of oil particles.[1,2] It is to be noted that the addition of $K_4Fe(CN)_6$ increased the original negative charge between the oil and the water, while the addition of $BaCl_2$, $AlCl_3$, and $ThCl_4$ all reduced the negative charge, the latter two salts causing a positive charge between the particles and the solution. The effectiveness of the various chlorides may be well illustrated by the following figures:

TABLE VII

LOWERING OF ELECTROKINETIC POTENTIAL AT AN OIL-WATER INTERFACE PRODUCED BY THE ADDITION OF CHLORIDES

Electrolyte	Concentration Millimol/liter Necessary to Reduce ζ from 0.046 to 0.037
KCl	24
$BaCl_2$	0.45
$AlCl_3$	0.01
$ThCl_4$	0.005

[1] Ellis, *Z. physik. Chem.*, 78, 321 (1912).

[2] Powis, *ibid.*, 89, 91 (1915).

The pronounced effect on ζ of the higher valence salts may be readily explained by the increased positive charge carried by the cations. Assuming that the distribution of the above four chlorides is the same at the oil water interface, and further that such a distribution is governed by the ordinary laws of adsorption, it is possible to account satisfactorily for the above behavior by means of the following diagrammatic curves:

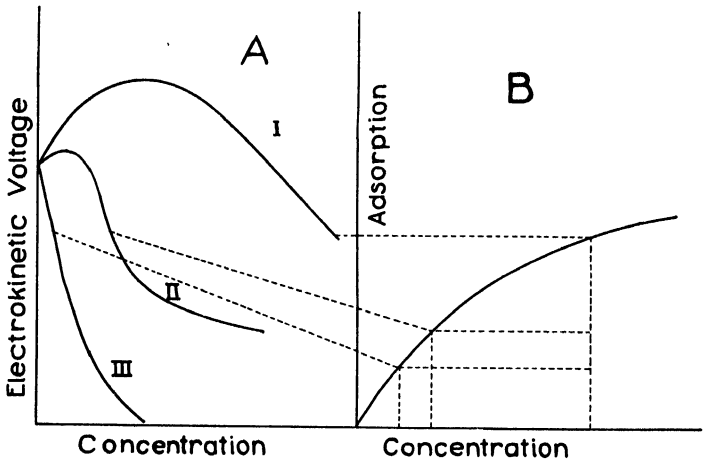


FIG. 10

Fig. A expresses the effect of various concentrations of uni- (I), bi- (II), and tri- (III) valent cations on ζ. Fig. B represents an ideal adsorption curve using the concentrations in the same units and scale as in Fig. A. It is to be noted further that, in Fig. B the adsorption of all three salts is assumed to be expressed by the same curve. From the diagram it is seen that by taking $\frac{1}{2}$ the quantity of a bivalent, and $\frac{1}{3}$ the amount of a trivalent as equal to unit quantity of a monovalent cation, a satisfactory explanation is given for the powerful effect of the cations of higher valence on ζ.

There are therefore two factors that influence ζ in the case of dissolved electrolytes, first the valence of the ion of the opposite charge of the wall, and secondly the extent of adsorption of the ion in question. Dyestuffs that are known to be highly adsorbed are also most effective in influencing ζ to a high degree.

ADSORPTION FROM LIQUIDS

When certain substances are brought in contact with gases or matter in solution, it is found that the latter substances adhere to the surface of the former. This phenomenon is called adsorption and is to be distinguished from absorption by the fact that the adsorbed materials are present at the surface of the adsorbent, while in the case of absorption the materials taken up penetrate throughout the body of the absorbing agent. Adsorption has attracted

TABLE VIII

ELECTROKINETIC POTENTIALS OF VARIOUS MATERIALS AGAINST WATER

Substance	Diameter of Particle	Mobility cm./sec.	ζ Volts
Arsenious Sulphide [1]	Less than 50 $\mu\mu$	$2.2 \cdot 10^{-4}$	− 0.032
Quartz [2]	1 μ	$3.0 \cdot 10^{-4}$	− 0.044
Gold [3]	Less than 100 $\mu\mu$	$4.0 \cdot 10^{-4}$	− 0.058
Platinum [3]	" " "	$3.0 \cdot 10^{-4}$	− 0.044
Ferric Oxide [2]	" " "	$3.0 \cdot 10^{-4}$	+ 0.044
Silver [3]	" " "	$2.4 \cdot 10^{-4}$	− 0.034
Bismuth [3]	" " "	$1.1 \cdot 10^{-4}$	+ 0.016
Lead [3]	" " "	$1.2 \cdot 10^{-4}$	+ 0.018
Iron [3]	" " "	$1.9 \cdot 10^{-4}$	+ 0.028
Oil	2 μ	$3.2 \cdot 10^{-4}$	− 0.046

a great amount of attention, due to the peculiarities of the theoretical problems presented, and, at the same time, the utilitarian aspect of the phenomenon is so important that many investigators have been enlisted with the practical application in mind.

One of the clearest methods of understanding the theoretical aspects of the problems of adsorption is contained in the following brief analysis: Let us contrast the three phenomena of chemical combination, true solution, and adsorption. The first is characterized as being entirely due to the attractive forces between the atoms or molecules. For example, if lime and solutions of sulphuric acid are brought together, the retention of the sulphuric acid may be readily predicted from the ordinary laws of chemical combination. True solution, on the other hand, is a phenomenon of simple mixing of molecules, i.e., it is a manifestation of the tendency of the thermal agitation of the molecules to produce a chaotic mixture. For example, let us consider a solution of iodine in water being shaken with a second immiscible solvent, say benzene. It cannot be said that the benzene either combines with or adsorbs the iodine from the aqueous solution. The whole question is clarified when treated as a case of solubility of iodine in water and benzene. Adsorption, on the other hand, is a manifestation of both of the above causal factors, i.e., molecular attraction and the kinetic motion of the molecules. The whole situation may be concisely expressed by the following set of curves, Fig. 11.

The ordinates represent the concentration, on the first phase, of the material that is being distributed between the two phases, while the abscissæ express the concentration of the same substance in the second phase. In case I (chemical combination) $X = k$, i.e., the law of definite proportions is obeyed. In case II (solution) $X/Y = k$, Henry's law of solubility is found to hold. While in case III (adsorption) $X/Y = k^{1/n}$, i.e., k is given an exponent inter-

[1] Quincke, *Pogg. Ann.*, **113**, 513 (1861).
[2] Whitney and Blake, *J. Am. Chem. Soc.*, **26**, 1339 (1904).
[3] Burton, *Phil. Mag.*, (6) **11**, 425 (1904).

mediate between 0 and 1, the values that are found to hold in the case of chemical combination and solubility respectively.

We have elected to discuss adsorption from liquids for the reason that such phenomena may be more easily connected with the surface energy relations that have been mentioned in the preceding section. This is due to the fact that only in the case of liquids are we able to measure directly the surface tension; however, as we shall soon discover, the surface tension must be that at the boundary between the adsorbent and adsorption medium (interfacial tension), and this may be directly measured only in the case of liquid adsorbents.

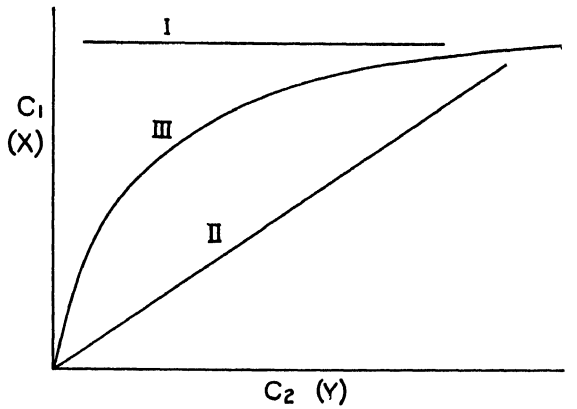


FIG. 11

In order to relate adsorption with the changes in surface tension that take place at a given interface, the well-known Gibbs' equation furnishes the most direct method. The law of adsorption may be most readily derived by means of the following thermodynamical cycle:[1]

Starting with a volume of solution V, of surface tension σ, surface ω, and osmotic pressure P, we first allow the surface to increase under constant volume, then the volume is increased without changing the surface. Finally the original surface and volume are restored.

The various steps in the process may be detailed thus:

(i) Let the adsorbing surface of area ω be increased to $\omega + d\omega$ whilst V remains constant. The work done is

$$\delta A_1 = -\sigma d\omega.$$

At the same time the osmotic pressure changes from P to $\left(P + \frac{\partial P}{\partial \omega} d\omega\right)$.

(ii) Let the volume of the solution be increased from V to $V + dV$ whilst

[1] Cf. Partington, Thermodynamics, Van Nostrand Co., 1924.

the surface remains unchanged. The work done is

$$\delta A_2 = \left(P + \frac{\partial P}{\partial \omega} d\omega \right) dV,$$

whilst the tension alters from σ to $\left(\sigma + \frac{\partial \sigma}{\partial V} dV \right)$.

(iii) Let the surface be restored to its original area, ω. The work done is

$$\delta A_3 = \left(\sigma + \frac{\partial \sigma}{\partial V} dV \right) d\omega.$$

(iv) Let the volume be decreased by dV, when the initial state is restored. The work done is

$$\delta A_4 = - PdV.$$

As an isothermal and reversible cycle has been completed,

$$\sum A = 0.$$

Hence,

$$\delta A_1 + \delta A_2 + \delta A_3 + \delta A_4 = 0;$$

$$\therefore \quad \frac{\partial \sigma}{\partial V} = - \frac{\partial P}{\partial \omega}, \tag{35}$$

a most significant equation because of the fact that the right-hand term expresses the fact that the osmotic pressure of a solution is a function of the surface of the same. This can only mean that the concentration of a solution is not uniform throughout, but is different at the surface from the concentration in the interior of the solution. In other words, it is strictly incorrect to define concentration as being equal to n/V, where n represents the mass of the dissolved substance, the correct definition of concentration being

$$c = \frac{n - u\omega}{V}, \tag{36}$$

where u measures the excess or deficiency of solute per unit area of surface. By evaluating the differentials dc/dv, $dc/d\omega$, and dP/dc from the above equation and the simple osmotic pressure-concentration relation ($P = cRT$), it is possible to put the above differential equation in the form

$$u = - \frac{c}{RT} \frac{d\sigma}{dc}, \tag{37}$$

which is known as the Gibbs' adsorption law. It is to be noted that u is positive when the surface tension is decreased by increasing concentration of solute. Therefore, a solution exhibiting a lower surface tension than the pure solvent will have the solute concentrated at the solution—air interface. From this it does not follow that the solute would necessarily be adsorbed on every sub-

stance added to such a solution. What takes place at the interface between the adsorbent and the solution can only be predicted on the basis of the interfacial tensions at such an interface. Inasmuch as it is impossible to measure directly the interfacial tensions between a solid and a liquid, test of the Gibbs' adsorption law must be limited to liquid adsorbents. With the latter, we are further confronted with the practical difficulty of obtaining a large and known surface. It is therefore apparent that the practical application of this theory is attended with many difficulties of such a nature as to make it of little value from a quantitative standpoint. Qualitatively, however, the above law allows one to predict whether adsorption at a given interface will be positive or negative from a knowledge of the surface tension changes at the interface in question. Frequently the mistake is made of measuring the surface tension at one interface and utilizing such results to predict the adsorption at another interface.

Lyophobe Colloidal Solutions

An examination of a number of colloidal solutions will reveal certain peculiarities that serve to distinguish them from true solutions. They are, as a class, unstable, show low diffusion coefficients, their colligative properties are only slightly different from those of the pure dispersion medium, they show the Tyndall phenomenon, have pronounced colors that are susceptible to wide variation, and are frequently of high viscosity, some exhibiting even marked form elasticity. All these phenomena are readily associated with the idea of a disperse phase of greater than molecular magnitude. In other words, the large size of the particle in suspension is sufficient to account for the Tyndall phenomenon, the slow diffusion, etc. A closer examination, however, will show that the mere assumption of increased size of the disperse phase is insufficient in itself to explain all the properties of colloidal solutions. There exist differences in behavior that do not admit of explanation on any simple basis of particle size. For example, an aqueous solution of gelatine must be regarded as a colloidal solution on the ground of its low diffusion coefficient, Tyndall effect, viscosity, and other properties. Contrasted, however, with a colloidal solution of gold or As_2S_3, it is apparent that there must exist some fundamental difference between the two solutions. The latter sols are very sensitive to electrolytes, can only be prepared in relatively small concentrations, are only slightly more viscous than the dispersion medium, and do not set to clear gels. Such differences were clearly recognized by all investigators, and numerous names have been proposed to designate the two classes of colloidal solutions. The nomenclature of Perrin is perhaps the most clearly in accord with the causal factors underlying the differences, and will therefore be adopted in this summary. Perrin called all sols that exhibited little tendency to become hydrated or solvated, lyophobe, and all others that showed a great tendency to unite with the dispersion medium, lyophile sols. Sometimes the expressions suspensoid and emulsoid are used in the same sense.

Most progress has been made in the theoretical development of the former class of sols and they will therefore receive first consideration here. Assuming

that lyophobe sols are unstable in the presence of small concentration of electrolytes, it is evident that if prepared by the formation of insoluble substances by metathesis the concentration of electrolytes at the end must not exceed that sufficient to precipitate the sol. For example, silver bromide sols may be prepared from solutions of silver nitrate and potassium bromide provided the concentration of the potassium nitrate at the end does not exceed the coagulation value. Arsenious sulphide sols lend themselves to easy preparation from the fact that arsenious oxide is sufficiently soluble in water so that treatment with hydrogen sulphide will give the sulphide without the formation of any electrolytes.

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

A necessary criterion for the preparation of a colloidal solution is that the disperse phase must show an exceedingly small solubility in the dispersion medium. Otherwise, due to the enhanced solubility of the highly convex particles, the system would soon revert to a true solution from which crystals would separate as saturation was reached.

The colligative properties of lyophobe sols may be disposed of in a very few words. The enormous molecular weight of the disperse phase results in an exceedingly small mole fraction of solute and therefore one should expect little variation from that of the solvent in either vapor pressure, boiling point, freezing point, or osmotic pressure. For example, an As_2S_3 sol made up of particles 5 $\mu\mu$ in diam. containing 50 gm. As_2S_3 per liter, which is a very concentrated lyophobe sol, would possess a mole fraction of As_2S_3 equal to

$$\text{moles of } As_2S_3 = \frac{50}{N \cdot \frac{4}{3}\pi r^3 (d - d_m)}$$

$$= 0.6 \text{ micromoles/liter;}$$

$$\text{mole fraction of } As_2S_3 = \frac{0.6 \times 10^{-6}}{55.5} = 1.08 \times 10^{-8}.$$

This calculation indicates clearly why the colligative properties of the lyophobe sols are so nearly equal to the dispersion medium itself. The lowering of the freezing point is of the order of a few thousandths of a degree, while the osmotic pressure calculated from the above molar concentration is only a few centimeters of water.

This last fact enables one to separate easily the disperse phase from the solvent by aid of a slight pressure provided one has a membrane that is impermeable to the colloid. Inasmuch as the diffusion of the colloid is very low and, furthermore, is greatly reduced through most membranes, the separation of the disperse phase from the dispersion medium becomes an operation that is easily realized experimentally.

The separation of colloids from substances held in true solution by means of a membrane that is impermeable to the former is termed dialysis, and was one

of the first distinctions between a true and a colloidal solution. In its theoretical aspect it is simply a question of diffusion rates, the colloidal being more sluggish in its movements and furthermore more influenced by the membrane. The diffusion of the true solute is effected by maintaining a concentration gradient through the membrane this being accomplished by frequently changing the solvent on the opposite side of the membrane.

If the separation of the colloid and dispersion medium is brought about by pressure through a membrane impermeable to the colloid, the operation is called ultra-filtration. From the calculation of the osmotic pressure of the lyophobe sols it is evident that a very small pressure is sufficient to bring about a separation from the solvent. The extension of this method should prove a fruitful field in many branches of chemistry; this is especially true in analytical chemistry where the separation of semi-colloidal precipitates often becomes a troublesome problem.

So far we have considered the colloidal system as if made up of a disperse phase and a dispersion medium, the former being always regarded as a pure substance. As a matter of fact, careful analysis always discloses the fact that the disperse phase is never pure, but usually has associated with it a certain amount of impurity. With arsenious sulphide, polysulphides are always found; silver oxide is always associated with colloidal silver, etc. The whole particle together with its associated "impurity" is termed the micelle. The stability of the sol is largely a matter of the composition of the micelle, it being known that it is practically impossible to prepare a stable lyophobe sol that consists of a pure substance dispersed in a pure dispersion medium. The composition of the micelle depends upon the composition of the surrounding solution. In the case of ferric oxide sols it is known that the micelle consists of Fe_2O_3 together with a certain amount of chloride. If the sol is subjected to ultra-filtration and the chloride composition of the filtrate determined, an increase in the latter concentration brings about an increase in the chloride content of the micelle. This is shown by the experiments of Maffia.[1]

TABLE IX

DISTRIBUTION OF CHLORIDES BETWEEN THE MICELLE AND INTERMICELLAR LIQUID OF A FERRIC OXIDE SOL.

$\alpha = 1.539, \quad 1/n = 0.268$

Cl Content of Filtrate	$a = \frac{\text{millimol Cl}}{\text{gm. } Fe_2O_3}$	a Calculated
.65	1.36	1.37
.82	1.47	1.46
.90	1.51	1.50
1.07	1.58	1.57
1.21	1.62	1.62
1.38	1.67	1.68
1.55	1.73	1.73

[1] *Koll. chem. Beiheft.*, **3**, 85 (1911).

The last column represents the chloride content of the micelle as calculated from the adsorption formula

$$a = 1.539c^{0.268}.$$

The above facts are of the utmost importance for a proper understanding of the stability of colloidal solutions and of their electric charge, and fo· an insight into the phenomenon of the adsorption from solution. The latter effect when reference is had to the adsorption of electrolytes occurs to such a minute extent per unit surface of adsorbent that ordinarily it escapes detection. But, in the case of a colloidal system, the surface of the disperse phase is so large that the net adsorptive effect becomes measurable. The surface increases rapidly with decreasing size of particle due to the fact that the volume of a spherical particle is proportional to the cube of the radius while the surface varies as the square of the same. The specific surface or surface per unit weight of disperse phase varies inversely as the cross section and in the case of particles of a few $\mu\mu$ in diameter assumes enormous magnitudes.

When a beam of light passes through a medium that contains particles small in comparison with the wave-lengths of light, it is observed that a certain diffused light is radiated from the medium. This phenomenon, which was first noticed by Tyndall,[1] is responsible for our ability to detect with the ultramicroscope a heterogeneity smaller than the dimensions of light waves. Rayleigh [2] gave the theory of this effect in its present form by considering that the colloidal particles "loaded" the ether. The diffused light is plane polarized and thus may easily be distinguished from fluorescence. Furthermore, Rayleigh showed that the intensity of such scattered light was inversely proportional to the fourth power of the wave-length of light, which fact explains why the blue rays are predominant in such light. This also accounts for many sols being bluish in reflected and yellowish by transmitted light. The intensity of the scattered light depends primarily upon the volume of the disperse particles, increasing with increasing size of the latter. The effect is also related to the refractive indices of the disperse phase and dispersion medium and must therefore be carefully studied from a physical standpoint to be fully appreciated.

It is the diffused light which is seen in the ultramicroscope and which enables the experimenter with such an instrument to deduce the existence of a particle in the optical field. This is the basis of the method of determining the size of colloidal particles with the aid of the ultramicroscope. The number of particles in a given solution is determined by counting the number present in the actual volume in the optical field. The ratio of the total volume to the volume in the optical field gives the factor that enables a calculation of the total number of particles to be made. The equation

$$l = \sqrt[3]{\frac{A}{d \cdot n}}, \tag{38}$$

[1] Tyndall, *Phil. Mag.*, (4) **37**, 384 (1869).

[2] Rayleigh, *Phil. Mag.*, (4) **41**, 107, 274, 447 (1871).

where A is the weight of particles in given volume, n the number of particles in a given volume, and d the density of the particles, permits an evaluation of the length of the side of the particle, assuming the same to be cubical in form.

The color of colloidal solutions is dependent upon the scattered light, but, in the majority of cases, the intensity of this light is small compared with the light absorbed by the particles themselves. In other words, the Tyndall light usually is of secondary importance in determining the color of colloidal solutions, the greatest effect coming from the specific absorption effects of the particles themselves. This fact is well illustrated by the following curves, which represent the measurements of diffused and transmitted light of a gold sol.

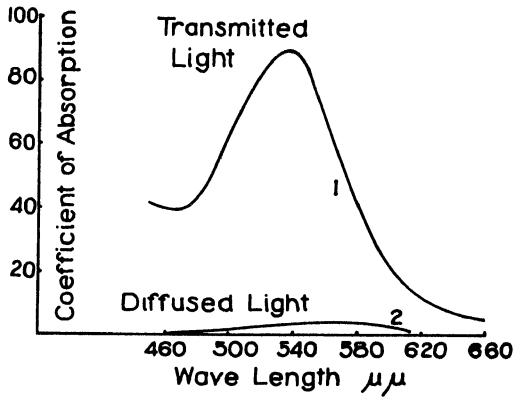


FIG. 12

There is a strong absorption band in the green which accounts for the red color of the sol. Curve 2 also indicates the relatively small effect due to the diffused light, thus clearly proving that the specific absorption of the solution is of far the greater importance in determining the color of the sol.

Coagulation of Lyophobe Sols by Electrolytes: One of the most important chapters of colloidal chemistry concerns itself with the phenomena that result from the addition of electrolytes to lyophobe sols. A perfectly stable sol when treated with a sufficiently strong solution of an electrolyte will give evidences of instability and will finally precipitate the disperse phase at the bottom of the containing vessel. This coagulation or flocculation of the sol is usually a gradual change, and may be best studied by measuring the rate of the coagulation. Unfortunately, such measurements are not easily carried out; the best method depends upon a determination of the size of particle with the ultramicroscope. This method does not lend itself to all solutions and is at best a laborious and time-consuming operation. Therefore, most investigators [1] have studied the minimum concentration of electrolyte (threshold value) necessary to bring the sol to a certain arbitrary stage of coagulation. Instead of determining the whole course of the coagulation, they have simply selected one point on the coagulation-time curve and determined the quantity of electrolyte necessary to bring the system to that point. Such a procedure is obviously theoretically inadequate in many ways and it is only recently that more attention has been paid [2] to the phenomenon from the standpoint of rate of coagulation.

[1] Freundlich, *Kolloid. Z.*, **1**, 321 (1907), *Z. physik. Chem.*, **73**, 385 (1910).

[2] Zsigmondy, *Gott. Nachr.* (1917).

It has been demonstrated that the addition of the electrolyte does not influence the Brownian motion of the colloidal particle per se, but rather the electrolyte removes the barrier to the union of the particles upon collision. When observed under the ultramicroscope, before the addition of the electrolyte, the particles never appear to unite upon collision; as soon, however, as the electrolyte is present, a clumping is observed which increases until the particles become so large that they settle rapidly to the bottom of the vessel.

The following experimental threshold values have been obtained by Freundlich and his coworkers.[1] It is to be remembered that these values will vary according to the method and concentration of the sol, and are therefore not to be given any weight as absolute constants.

TABLE X

COAGULATION CONCENTRATIONS OF As_2S_3 SOL. (1.85 GM./LITER)

Electrolyte	Conc. millimol/liter
K_3 Citrate/3	>240
K Acetate	110
K Formate	86
LiCl	58
NaCl	51
KCl	49.5
KNO_3	50
$K_2SO_4/2$	65.5
HCl	31
$H_2SO_4/2$	30
Aniline Chloride	2.5
Morphine Chloride	0.42
Crystal Violet	0.165
Fuchsine	0.11
$MgCl_2$	0.72
$MgSO_4$	0.81
$CaCl_2$	0.65
$SrCl_2$	0.635
$BaCl_2$	0.69
$ZnCl_2$	0.685
$AlCl_3$	0.093
$Al(NO_3)_3$	0.095
$Al_2(SO_4)_3/2$	0.096
$Ce(NO_3)_3$	0 080

The above data may be taken as typical of the experimental facts from which one may deduce the general theory of the coagulation of lyophobe sols. The data are restricted in their significance, as outlined above, and must therefore be looked upon as of secondary importance when compared with the measurements of the rate of coagulation. However, it is possible to draw a number of important generalizations from the above facts. In the first place, it is to be noted that with a negatively charged colloid the valency of the cation is of primary importance in fixing the threshold concentration of the

[1] *Loc. cit.*, p. 41.

electrolyte. This rule is not always reliable for it is also to be noted that certain electrolytes containing univalent cations are more effective in bringing about coagulation than other bivalent cations. In addition, the influence of the anion is not entirely negligible for considerable variation is associated with changes in the nature of the same.

TABLE XI

COAGULATION CONCENTRATIONS OF Fe_2O_3 SOL. (.823 GM./LITER)

Electrolyte	(C.) millimol/liter
NaCl	9.25
KCl	9.0
$BaCl_2/2$	9.65
KBr	12.5
$Ba(NO_3)_2/2$	14.0
HCl	>400
$Ba(OH)_2/2$	0.42
K_2SO_4	0.205
Tl_2SO_4	0.22
$MgSO_4$	0.22
$K_2Cr_2O_7$	0.195
H_2SO_4	0.5

All the above observations may be correlated as follows: The micelle owes its charge and therefore its stability to the presence of a certain amount of adsorbed electrolyte. This material may be considered as constituting an ionic double layer that gives rise to the charge and the potential. The addition of other electrolytes to the inter-micellar liquid brings about a rearrangement of this adsorbed layer of the micelle, and, with it, a change in the potential difference. This change may be either an increase or decrease in the existing charge of the micelle. If the charge is diminished, then the opposition to impacts between particles resulting in a union is decreased and therefore the stability is diminished. It is obvious that the cations will be most effective in decreasing the negative charge of the micelle, and also that a strongly adsorbed univalent cation may be more effective than a weakly held polyvalent cation. Just as in the effect on the potential difference, here in the case of coagulation there is ever present the valence effect and the extent of adsorption of the various ionic species.

Freundlich and his coworkers [1] have experimentally proven most of the statements made in the above paragraph. They show in the first place that the most effective ion in bringing about coagulation is more strongly adsorbed by the colloid than an ion of lesser effect of the same valence. The following table illustrates the idea in a quantitative manner.

With the exception of the picrate the equivalent amounts adsorbed are the same, while the molar quantities differ widely but always parallel the threshold concentration. Similar experiments have been conducted with a great number

[1] *Loc. cit.*, p. 41.

TABLE XII

AMOUNTS OF ANIONS ADSORBED IN THE COAGULATION OF Al_2O_3 SOLS

	Threshold value $\frac{\text{millimol}}{\text{liter}}$	Millimol adsorbed per gm. Al_2O_3	Milli-equivalent per gm. Al_2O_3
Salicylate	8	.46	.46
Picrate	4	.275	.275
Oxalate	.36	.275	.55
Ferricyanide	.10	.14	.42
Ferrocyanide	.08	.11	.44

of sols and with various coagulants,[1] and the result is always a substantiation of the above. That the equivalent quantity adsorbed should be the same is a significant fact and leads directly to the supposition that the coagulation results from the replacement of the ion in the micellar layer by another ion. This assumption would easily explain the inconstancy of the threshold values with various colloidal solutions, in other words the "purity" of the micelle determines the amount of added electrolyte necessary for coagulation.

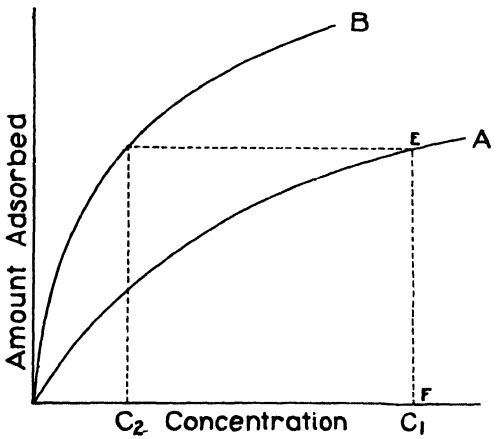


FIG. 13

The difference in coagulation value of two ions of the same valence but of unequal adsorption is strikingly brought out by a diagram illustrating the adsorption isotherm.

If A be the adsorption isotherm of one electrolyte and B that of the other, let us assume that an amount of A equal to the ordinate EF be necessary to bring about coagulation. A similar quantity being required in the case of B would demand the concentration of the intermicellar liquid to be C_2 instead of the much higher value C_1 that is demanded of substance A.

By means of a similar diagram it is possible, also, clearly to indicate the increased effect of the polyvalent ions.

The ordinate A representing the amount necessary to produce coagulation with the univalent ion, $\frac{1}{2}$ and $\frac{1}{3}$ of this amount gives the quantities of the bi- and trivalent ions respectively assuming equal adsorption for all. The corresponding threshold concentrations are C_1, C_2 and C_3.

[1] Freundlich, *Kapillarchemie*, p. 576 (1922).

Rate of Coagulation: A very important chapter in the theory of colloids was opened by the experimental observation of Zsigmondy on the rate of coagulation of gold sols.[1] He rapidly mixed 50 cc. of a red gold sol with 50 cc.

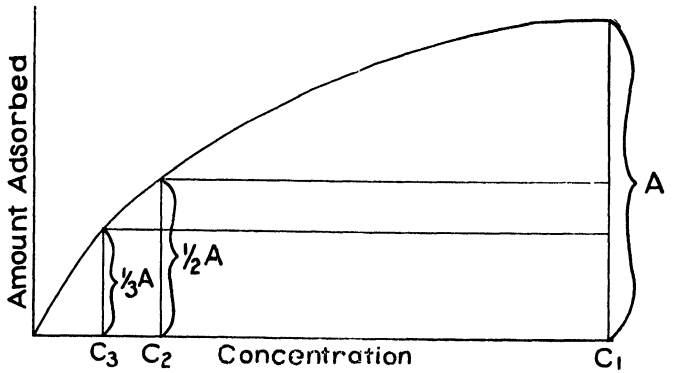


FIG. 14

of an electrolyte solution and noted the time in seconds for a certain color change to take place, which change was taken as indicative of the progress of the coagulation. His results with $SrCl_2$ as the coagulating electrolyte are summarized in the following curve.

For the time being we shall concentrate our attention upon the vertical portion of the curve, the significance of which is striking. Other electrolytes give similar curves, the vertical portion occurring at exactly the same time. This indicates that when a certain concentration of electrolyte is present the coagulation velocity is a constant. Furthermore, this rate is entirely independent of the nature or the concentration of the electrolyte after this point is reached. This region of rapid coagulation has been satisfactorily explained by Smoluchowski [2] on the basis of the Brownian motion. The latter's analysis, which constitutes a most beautiful application of the kin-

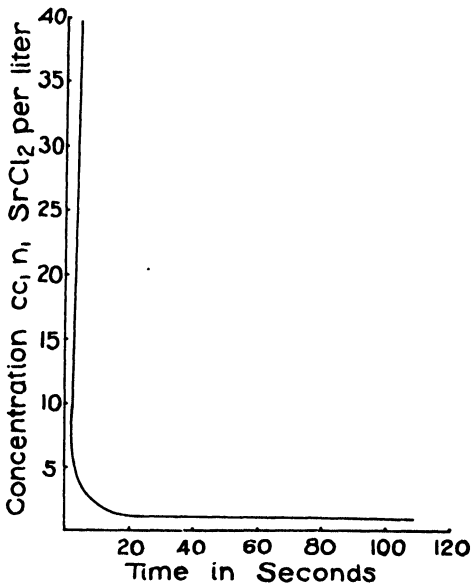


FIG. 15

[1] *Gott. Nachr.*, p. 41, (1917).

[2] v. Smoluchowski, *Phys. Z.* **17**, 557, 583 (1916); *Z. physik. Chem.*, **92**, 129 (1917).

etic theory, results in a qualitative and quantitative explanation of the rapid coagulation that is worth serious study by all chemists. Smoluchowski considers that in the region of rapid coagulation the particles are completely discharged and in this state each impact between particles results in the formation of a larger particle. These secondary particles in turn unite with other primary and secondary particles to form still larger units. According to Smoluchowski, the total number of particles in volume V at time t after the beginning of the coagulation equals

$$\sum \nu = \nu_1 + \nu_2 + \nu_3 \cdots = \frac{\nu_0}{1 + \beta t},$$

where ν_0 is the number of particles originally present in volume V and ν_1, ν_2, ν_3 the number of primary, double, and triple particles at time t, β having the value $4\pi\nu_0 DR$, D being the coefficient of diffusion. Furthermore, Smoluchowski defines the time of coagulation as the time necessary to reduce the number of primary particles to $\frac{1}{4}$ their original number, or the total number of particles to $\frac{1}{2}$ the number before the beginning of coagulation, i.e.,

$$T = 1/\beta = \frac{1}{4\pi DR\nu_0}.$$

The results of this analysis may be conveniently presented by a graphical chart.

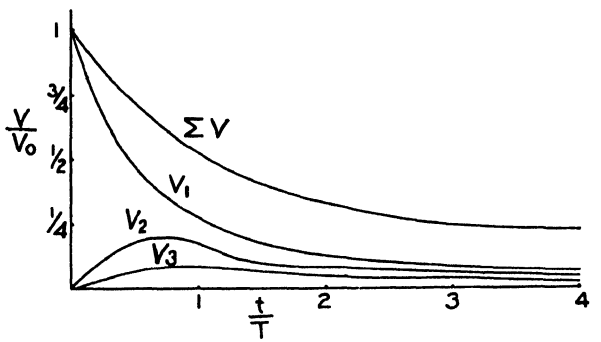


FIG. 16

Smoluchowski's theory has been verified by a number of experimenters,[1, 2] the methods employed being the determination of the number of particles at various times by means of ultramicroscopic observations.

It is interesting to note that Smoluchowski has calculated that if a chemical reaction were to proceed by the same mechanism, i.e., each collision resulting in a new product, a concentration of $\frac{1}{3} .10^{-9}$ equivalents per liter would suffice to bring about a conversion of $\frac{3}{4}$ of the reactants in one second. Inas-

[1] Westgren and Reitstötter, *Z. physik. Chem.*, **92**, 750 (1918).

[2] Arkel, *Rec. trav. chim.*, **39**, 656 (1920).

much as many chemical reactions do not proceed at this rate, the supposition is that collisions must take place in some specific manner in order to account for the slow rate.

The coagulation of colloids also may take place at slower rates than have been considered. This fact is well proven by Zsigmondy's experiments with the lower concentration of electrolyte solutions. The region of slow coagulation has also been the object of considerable study but it cannot be said that the conclusions are in sufficiently definite form to warrant discussion in a brief summary such as this. Of course, the assumption made is that the particle is not completely discharged, which fact results in only a certain fraction of the collisions forming new particles.

Lyophile Colloidal Solutions

It is possible to obtain fairly correct conceptions of the various factors that determine the properties of the lyophobe class of colloidal solutions, or more definitely, with the aid of the principles of thermal agitation, adsorption, and electrical charge a more or less rational explanation of the properties of such sols may be formulated. In dealing with the other class, the lyophile, there is immediately felt the crying need for guiding generalizations. It is generally accepted that such sols, as distinguished from the lyophobe, are more closely related to the dispersion medium, i.e., the disperse phase is hydrated or in combination with the solvent. While this explanation is undoubtedly the reason for the peculiar behavior of such systems, a quantitative insight into the properties of the lyophile sols cannot be had until we understand much more of the nature of solvation or hydration.

This section of colloidal chemistry may therefore be said to be in almost a purely empirical state. There is no guiding generalization except the vague idea of solvation, which is imperfectly understood. Nevertheless, a vast amount of data has been collected regarding such sols, and a statement of the more important observations will form the basis of the following discussion:

Lyophile sols are characterized by

1. Stability in fairly concentrated solutions of electrolytes.
2. High viscosity, often exhibiting elastic properties.
3. Difficulty of being resolved under the ultramicroscope.
4. Setting to gels.

The above characteristics, together with other minor ones, serve to distinguish such solutions from the lyophobe class. The latter solutions show the opposite behavior in all the above four points and therefore may be regarded as being fundamentally different in nature. It must be constantly borne in mind that these two great classes of colloidal solutions are connected by a class of intermediate solutions that show some of the properties of both classes. In other words, the distinction between the two groups is not always sharp, but may be made difficult in certain cases. For example, aluminium hydroxide sols show many of the properties of the lyophiles but are nevertheless classed

as lyophobe due to their sensitiveness to coagulation by electrolytes. Furthermore, it is often possible to convert a distinctly lyophile sol into a characteristically lyophobe, by changing the dispersion medium. In this case it is obvious that it is possible to arrest the change in the nature of the medium at such a point that the system will exhibit the properties of both classes to a certain degree.

With both types of solutions, there is, however, a disperse phase of greater than molecular dimensions. In the case of the lyophile systems this conclusion is drawn from their small diffusion coefficients and their low osmotic pressures. The ultramicroscopic channel of investigation is practically closed with this type of sol due to the small difference between the refractive indices of the two phases. Further, the stability in the presence of electrolytes shows that they do not possess a well-defined electric charge, which fact is well illustrated by the inability of the ordinary electrokinetic phenomena to furnish much helpful information. In addition, most of these colloids are composed of substances that are much more chemically active than those comprising the lyophobe class, there being always therefore the possibility of such changes beclouding the ordinary colloidal reactions. In the light of the above it is not to be wondered at that this chapter of colloidal chemistry is at present in a most unsatisfactory state from a theoretical standpoint.

The ordinary aqueous lyophile colloids are represented by such substances as gelatine, sulphur, silicic acid, stannic acid, various albumens, starch, soaps, and many dyes.

Viscosity: One of the outstanding properties of such colloids is their high viscosity as compared with water, and the changes in viscosity that take place with the concentration and the age of the sol. It has also been observed [1] that the measurements of viscosity are not comparable when made with different types of viscosimeters. The differences are so great as to indicate that something other than viscosity is being met with in this class of solutions. Close investigation has shown [2] that the lyophile sols show a displacement elasticity which is not sufficiently pronounced to cause such systems to assume a form independent of gravity, but which does manifest itself in effecting a change in "viscosity" depending upon the shearing time of the method employed. This particular property has been ably investigated by Hatschek and his coworkers,[2] who have also evolved methods of measuring this elasticity. In the Ostwald viscosimeter the apparent viscosity of these sols will be found to increase as the rate of flow through the capillary is diminished, at high rates the measurements should more nearly approach the true viscosity.

Einstein has proposed [3] an equation to account for the increase of viscosity of a medium due to the introduction of a highly disperse phase. This relationship is derived from kinetic considerations and reads as follows:

$$\eta = \eta_0 (1 + 2.5\theta),$$

[1] Garrett, *Diss. Heidelberg*, 1903.
[2] Hatschek, *Kolloid Z.*, **13**, 88 (1913).
[3] *Ann. Physik.*, (4) **19**, 289 (1906).

η_0 and η being the viscosities of the pure medium and the colloidal solution respectively, while θ is the actual volume of the disperse phase. It is to be noted that this equation demands a linear increase of the viscosity with the concentration of the disperse phase, and also that the viscosity is independent of the size of the particles, being a function only of the total volume of the latter. Lyophobe colloids show a linear increase of viscosity with increasing concentration, but, unfortunately, the experimental evidence does not verify the coefficient 2.5. The lyophile colloids, on the other hand, show no agreement with the formula of Einstein. Hatschek has proposed [1] the following relation which has been found to fit his measurements, in which it is clearly seen that the increase of viscosity does not occur linearly with the concentration:

$$\eta = \frac{\eta_0}{1 - \theta^{1/3}} \cdot \tag{39}$$

There is also evidence available [2] with certain sulphur sols to show that the viscosity is a function of the size of the disperse particle. Einstein in attempting to reconcile the discrepancy between his theoretical conclusions and the experimental facts further assumes [3] an influence due to the electric charge of the particle.

Diffusion: The diffusion coefficient of most lyophile colloids is greater than that of the lyophobe class, nevertheless the measurements are difficult due to inability to utilize the ultramicroscope and thus directly determine the mean horizontal displacement ξ. However, it is possible to measure the diffusion coefficient by proceeding as in the case of true solutions, i.e., by actually determining the amount of material transferred into an adjacent layer of pure solvent. R. O. Herzog [4] has made such measurements with the following results:

TABLE XIII

DIFFUSION COEFFICIENTS OF LYOPHILE SOLS

	Temp.	D. cm./sec. $\times 10^5$
Egg Albumen	7.75	0.052
" "	15.5	0.063
Pepsin	12	0.073
Invertin	16.6	0.041
Emulsin	15.3	0.042
Urea	18	1.01
Glucose	18	0.57
Raffinose	18	0.355

It is to be noted that the diffusion of the colloids is much slower than that of the true solutes, values for which have been added for comparison. With

[1] Hatschek, *Kolloid Z.*, **12**, 238 (1913).
[2] Odén, "Der kolloide Schwefel," p. 102.
[3] *Loc. cit.*
[4] Herzog, *Z. Elektrochem.*, **17**, 679 (1911).

the aid of these numerical values of the diffusion coefficients it is possible to calculate the size of the lyophile colloidal particles.

$$D = \frac{RT}{N6\pi r\eta} \cdot \tag{40}$$

Substitution in this equation gives a value of the radius of egg albumen as 2.8 $\mu\mu$, which would indicate the molecular weight of the above compound to be 62,000. This figure was obtained with the aid of Avogadro's number and the product of the volume and density of the particle. The density is a somewhat questionable quantity, so that the above molecular weight is only to be regarded as an approximate value.

$$M = \tfrac{4}{3}\pi r^3 \delta N. \tag{41}$$

Osmotic Pressure: Closely connected with the question of diffusion is the osmotic pressure. This latter property is more pronounced with lyophile than with lyophobe sols because of the finer particle size of the former. The measurement of osmotic pressure is, however, frequently difficult, due to the inability to free the sol entirely of materials in true solution; these latter substances of course exert an appreciable pressure of their own, and furthermore this effect cannot be neutralized by the employment of intermicellar liquid on the pure solvent side of the membrane. The unequal distribution of electrolytes, according to the Donnan theory of membrane equilibrium [1], is the cause of the impossibility of correcting for the presence of electrolytic impurities in the sols, the osmotic pressure of which is to be measured.

The experiments of Hufner and Gansser with hæmoglobin from cattle [2] seem to have been sufficiently refined to warrant the belief that the measurements do actually reflect the osmotic pressure of the above substance in solution. Using a parchment membrane they measured an osmotic pressure of 109 mm. Hg at 1° with a 10.8 per cent solution. This pressure under the above conditions is that shown by a substance of molecular weight equal to 16,300. This figure is further verified by the determination of the amount of carbon monoxide taken up by hæmoglobin. Assuming that one mole of the latter combines with one mole of carbon monoxide, the molecular weight comes out as 16,700, a number that is in substantial agreement with that found by the measurements of the osmotic pressure.

Conductivity of Colloidal Electrolytes: Considerable information has been collected [3] regarding the nature of colloidal solutions by studying the electrical conductivity of the same. We have already spoken of cataphoresis as applied to lyophobe sols, which method when applied to lyophile colloids is not productive of results of much value. The conductivity of such solutions, differing again from the lyophobe class, is appreciable, and in the case of soap solutions

[1] Donnan, *Z. Elektrochem.*, **17**, 572 (1911). Cf. Chapter VII.

[2] *Arch. Physiol.*, 209 (1907).

[3] McBain and coworkers, *J. Chem. Soc.*, **117**, 530 (1920); *J. Am. Chem. Soc.*, **42**, 426 (1920).

has yielded important insight into the makeup of colloidal electrolytes. This field has been largely investigated by McBain, who is also responsible for an interpretation of his experimental results that gives evidence of being of great value with many other lyophile systems.

The specific conductivity is quite large and according to McBain is constant and easily reproducible. The following table shows the specific conductivity λ and the equivalent conductance Λ of sodium palmitate at 90°.

TABLE XIV

CONDUCTIVITY OF SODIUM PALMITATE SOLUTIONS AT 90°

C. mole/1000 g. H_2O	λ	Λ	Degree of Hydrolysis
0.01	0.001319	137.0	0.066
0.05	0.004210	88.61	0.0222
0.1	0.007723	82.51	0.0128
0.2	0.01199	82.38	
0.347	0.02657	87.04	
0.5	0.03748	89.48	0.0037
0.75	0.05210	87.48	0.0030
1.0	0.06263	84.66	0.0020

It was formerly assumed that the high specific conductance of the soap solutions was due to the carrying of the current by the NaOH formed by hydrolysis. McBain has proven that this explanation is untenable by his measurements of the degree of hydrolysis by means of P_h determinations. His results with the potassium salts of various fatty acids may be concisely expressed by $\Lambda - c$ curves, which are reproduced below. Curves from 1 to 7 refer to the acetate, capronate, caprinate, laurinate, myristate, palmitate, and stearate respectively.

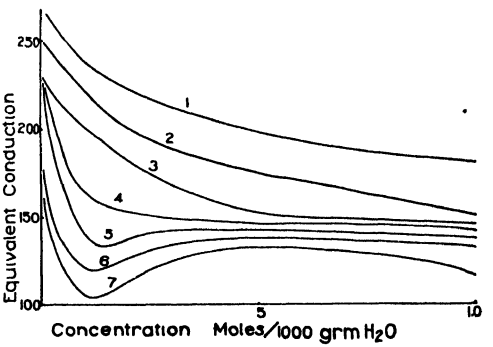


FIG. 17

McBain's explanation of the abnormal increase of equivalent conductivity observed with the higher fatty acid salts is that the latter give rise to colloidal anions of high mobility. The increase in mobility is explained by the following considerations: In the cataphoresis experiments the velocity of the moving charged particle was shown to equal

$$u = \frac{\zeta HD}{4\pi\eta}, \tag{42}$$

where the previous meanings of the symbols are retained (p. 1296). The velocity, therefore, is independent of the radius of the particle. The physical law relating the charge to the potential of concentrically charged spheres of radius r and r_1, is

$$\zeta = \frac{e(r_1 - r)}{Drr_1} = \frac{e\delta}{Dr(r + \delta)} \cdot \tag{43}$$

Inasmuch, however, as ζ with most stable particles does not differ much from the constant potential (50–70 millivolts), it follows from the last equation that the charge of a colloidal particle must increase with increasing size of the latter. The same reasoning may be applied to the mobility of the ions, only in this case a charged isolated sphere must be assumed instead of concentric spheres as demanded by the Helmholtz double layer. With the ions, the relation then becomes

$$\zeta = \frac{e}{Dr} \cdot \tag{44}$$

Taking the radius of the ion to be from $2\text{–}3 \times 10^{-8}$ cm. and the charge per ion as that calculated from Faraday's law, ζ turns out to be from 60–90 millivolts. This represents a truly astonishing result—namely, that the potential of an ion against the surrounding medium is practically identical with that of a colloidal particle. From the above equation it also follows that, as the ion becomes larger, the potential must decrease, inasmuch as the charge per ion cannot vary.

McBain makes the assumption that the anion is a colloidal complex in which are a number of simple anions each of which carries its normal charge. This multiple charge when distributed over the large surface of the colloid is sufficient to raise ζ to a value that makes for increased mobility notwithstanding the fact that the frictional opposition is increased with the larger particles.

McBain also determines [1] the composition of his soap solutions in terms of the various molecular and colloidal species by means of indirect vapor pressure measurements—a refined dew point method was employed. The results of these measurements together with his conductivity values permitted him to make approximate calculations of the amounts of the various constituents of the solutions.

Isoelectric Point: The colloidal behavior of albumenous substances has been made the object of study by countless investigators. Here the problem is complicated by the chemical activity of the materials. J. Loeb has contributed [2] very greatly to clarifying this mass of material by his emphasis on the purely chemical phase of the problem. For example, this worker regards gelatine as an amphoteric substance that, under certain conditions, is capable

[1] McBain and Salmon, *Proc. Roy. Soc.*, **97A**, 44 (1920).

[2] Loeb, Proteins and the Theory of Colloidal Behavior (1922).

of combining with acids and under others with bases to form true salts. The criterion as to whether the basic or the acidic property be uppermost is the P_h of the substance. Thus, for example, when gelatine is treated with acid of a certain strength and thereby brought to a definite P_h value, it may form a salt with gelatine as the cation or anion depending upon the particular P_h that was selected. At the isoelectric point, i.e., where the basicity equals the acidity, the substance does not combine either with acids or bases. If the acidic ionization of the substance be expressed

$$K_A = \frac{(ROH^-)(H^+)}{(HROH)}$$

and the basic ionization by the equation

$$K_B = \frac{(HR^+)(OH^-)}{(HROH)},$$

at the isoelectric point,

$$(HR^+) = (ROH^-).$$

Therefore,

$$(H^+) = [(K_A/K_B).K_W]^{1/2},$$

K_W being the ordinary dissociation constant of water. This relationship allows one to predict the position of the isoelectric point, i.e., the P_h value of the same, from a knowledge of the strengths of the acid and the base in the amphoteric substance.

Loeb shows that most of the properties of albumenous colloids are in intimate relation with the P_h of the same, and he also points out that most of the confusion in the early work is due to failure to prepare materials of definite P_h value. He furthermore extends his views with the aid of the Donnan theory of membrane equilibrium to explain the variation of the osmotic pressure with the P_h of the solution. Space does not permit a description of his experimental methods or a detailed discussion of his results, but the work is of great importance to all interested in problems associated with amphoteric colloids.

From the brief enumeration of some of the important members of the class of lyophile colloids it can be seen that such substances are numbered with those that must be regarded as of the utmost importance in the life of man. That our theoretical knowledge of such solutions is limited is not due to a lack of effort, but rather must be attributed to the complexity of the problems involved. Not only are the particles colloidal in dimension, but they are not homogeneous, nor are they to be regarded as being chemically inert.

Perhaps it may be well in closing this brief summary of the colloidal state of matter to impress the reader once more with the fact that colloidal systems

are in metastable equilibrium. They are only transient stages between that of true solutions and crystalline solids. These two extremes typify absolute randomness on the one hand, and an orientation on the other (that is so searching as to result oftentimes in the disappearance of the molecule as a structural unit). In the light of this, it is evident that the study of rate becomes of prime importance with such systems. A careful and intensive investigation of the rates of the various colloid-changes will lead to a fuller appreciation of these most interesting systems.

CHAPTER XXI

RADIOACTIVITY

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The fundamental contributions to the science of physical chemistry that have resulted from the investigation of atomic disintegration and of the related phenomena have established such intimate relations between the two that it is no longer easy to segregate an independent subject matter which one may term radioactivity. The time has likewise passed when it is desirable in a brief chapter to adopt a historical order of presentation.

The modern conceptions of atomic structure and of progressive atomic change or evolution have already been discussed. It remains to consider the properties of the different radioactive elements, their genetic relationships and the character of the rays and particles emitted at the time of atomic disintegration.

Radioactive Series: The property of nuclear instability resulting in radioactive change belongs primarily to the elements of highest atomic mass. Only those elements of atomic mass greater than 210 possess distinct radioactive properties. Of the common elements, only two, uranium and thorium, are certainly radioactive. It is more than accidental that they have the two highest known atomic masses. Each of them constitutes the parent member of a series of radioactive elements genetically related. Actinium, an element discovered by radioactive methods, is the parent element of a third series, which appears to be genetically related to the uranium series. Reasons have been presented by Russell [1] for believing a fourth series remains to be discovered.

Rate of Atomic Change: The rate at which one radioactive element changes into the next lower in the series has been found by experiment to follow a very simple law. Of any quantity under consideration the same fraction always changes in unit time, or the rate of change is always proportional to the total quantity present. This is expressed by the ordinary logarithmic law:

$$N_t = N_0 e^{-\lambda t},$$

when N_0 is the initial number of atoms of one kind present (or quantity measured in any other units), N_t the number remaining after any interval of time t, and λ is a constant characteristic of the element in question. This is

[1] *Nature*, 112, 588 (1923).

the ordinary equation for a unimolecular reaction, and in fact represents the most perfect case, and, as is sometimes maintained, may represent the only true case of unimolecular change. The rate has been found to be independent of any conditions, physical or chemical, that have, so far, been imposed. In fact the ability to change λ constitutes the crux of the problem of the utilization of intra-atomic energy which has been pronounced the most important future problem of energetics.

The fraction changing per unit of time (λ) is the reciprocal of the average life (θ) of all the atoms of a given species. The half life period of a radioactive element is the time (T) required for half of any given quantity to undergo change.

$$T = \theta ln2.$$

The period of any radioactive element is its most fundamental physical constant. The different periods found among the various radioactive elements embrace an extraordinary range from 10^{-11} seconds to 10^{10} years. Some empirical relations have been found between λ and other constants, but the fundamental principles, doubtless involved in the little explored structure of the nucleus, are yet to be disclosed.

Radioactive Equilibrium: The rate at which one element changes into another or the relative periods of the members of a radioactive series of elements evidently control the quantities of the elements that can coexist. The shorter the life of a given element, the smaller the quantity that can coexist with its parent or offspring elements. The relations which exist may be variously classified according to the genetic distribution of elements with different life periods. One of the simplest and most important cases is that of a long-lived parent succeeded by a much shorter one. The latter will accumulate until the rate of its decay just counterbalances its rate of formation, when an irreversible dynamic equilibrium results—called radioactive equilibrium. For the case of a long-lived parent A_1 with period λ_1 of which N_1 atoms are present, the equilibrium quantities of element A_2, A_3, etc., are given by

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 \cdots,$$

or

$$\frac{\lambda_1}{\lambda_2} = \frac{N_2}{N_1}, \text{ etc.}$$

Thus, the equilibrium quantities are inversely proportional to the periods. This is a principle of first importance, since it means that only long-lived elements can be accumulated in large quantities and *vice versa*.

Another principle of importance in connection with radioactive equilibrium is one which for convenience may be termed "constant flux" of atoms. It follows directly from the definition of radioactive equilibrium that, in a series in equilibrium, the number of atoms of each kind undergoing change in unit time must be a constant. Since one α-particle is emitted per atom changing, the number of α-particles emitted per second is constant for equilibrium

quantities of all the elements in a series. It is therefore evident that much simplicity is effected by choosing a gram of one member in a series as the quantity unit and letting the quantities of other members of the series in equilibrium with 1 gram of the standard be designated by a common unit. It must be understood that these relations hold only in a straight series, where no branching occurs.[1]

Emission of Energy: One of the most striking properties of radioactive substances is the continued emission of energy in the form of high velocity particles the absorption of which results in the production of heat. It is now conceded that the ultimate source of this energy is the intra-atomic energy residing in the nucleus of the atom. Although its total quantity is unknown, it is quite evident that the portion liberated in a single atomic transition far exceeds the energy associated with ordinary chemical action. On this account there has been much speculation about the possibility of utilizing intra-atomic energy for power generation. Many fantastic statements have been made about the total heat evolved by 1 gram of radium during its entire life and how much work could be accomplished with it. While it is true that a battleship could be lifted with the total energy from a relatively small quantity of radium, it is impossible to change or control the rate of energy emission, and hence it is quite as hopeless for a gram of radium to expend all its available energy in one burst as it would be for a man to perform a herculean task by expending the total energy of his whole life in a single moment.

One remarkable result of the heat emission of radioactive substances is its effect in the earth's crust. The content of radium in the earth's crust is of the order $2\text{–}4 \times 10^{-12}$ gram per gram of rock, the corresponding uranium content is $6\text{–}12 \times 10^{-6}$; the thorium content is $1\text{–}2 \times 10^{-5}$. The total heat evolved is so great that it has been calculated to be much in excess of the radiation from the earth; hence, the earth must be becoming warmer instead of cooler. Joly has recently based a new theory of structural history of the earth's crust on the assumption that the earth passes through a succession of cycles, radioactively heating up owing to the poor conduction of the crust until it melts, then a period of more rapid heat loss until solidification again results and consequent thickening to a maximum thickness of about 30 km., then melting at the bottom, thinning until completely fluid and so forth through a series of cycles (cf. p. 1357).

α-Rays: One of the early accomplishments of Rutherford was the demonstration that an α-particle is a helium atom with a double positive charge, He^{++}. This is evidently the He nucleus. Owing to the high initial velocity of α particles (1/15 to 1/20 velocity of light), one would expect that the two electrons associated with ordinary helium could not accompany it in this rapid flight. Henderson [2] has just shown that in fact an equilibrium

$$He^{++} + \ominus \rightleftharpoons He^{+} + \ominus \rightleftharpoons He$$

[1] N. E. Dorsey, *J. Wash. Acad. Sci.*, **11**, 381 (1921).

[2] Henderson, G. H., *Proc. Roy. Soc.*, **102A**, 496 (1923). Rutherford, *Phil. Mag.*, **47**, 277 (1924). R. H. Fowler, *ibid.*, **47**, 416 (1924).

represents the true state of affairs; in other words, an α-particle captures electrons and loses them again in its flight, and as its velocity diminishes the equilibrium is shifted toward neutral He.

Owing to its high velocity and mass of atomic dimensions the α-particle possesses great kinetic energy which renders it a powerful agent endowed with many unusual properties. Due to its charge and velocity it is deflected by powerful magnetic and electrostatic fields. By such deflection its e/m value was determined. Deflection of α-particles by atoms through which they pass has proved a most fertile means of studying atomic structure. The Rutherford theory of atomic structure resulted from his studies of deflections and nuclear encounters of α-particles.

As long as the velocity of the α-particle is great, it passes in a straight line through the electronic fields of a large number of atoms, removing electrons and thus producing ionization. Toward the end of the path when the velocity is becoming diminished, deflections from the straight line of flight result, termed *scattering*. Very rarely, a large deflection or reversal of direction occurs. The great rarity of this phenomenon led Rutherford to the present conception of the atom with a very minute nucleus. The total ionization per α-particle from different radioactive elements will be found in the tables for the different series. The distribution of ionization along the path of an α-particle from RaC is shown in Fig. 1. The path would be identical for any other α-particle of the same velocity. The initial velocity of all α-particles from a given kind of atom is identical. For α-particles with initial velocity less than that of RaC, the path is the same, beginning at the corresponding point in the path.

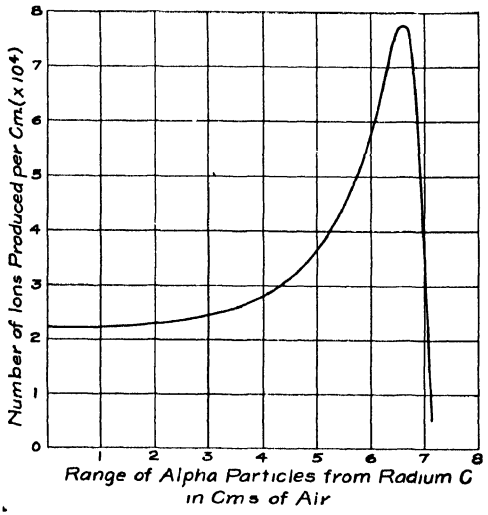


FIG. 1 The Distribution of Ionization

The range of the α-particle is the total distance it will traverse in a given substance until its energy is dispersed. See Tables V, VI and VII.

When an α-particle impinges on phosphorescent zinc sulphide, a scintillation is produced. The observation of these scintillations furnished the first definite evidence of the existence of individual atoms. The enumeration of scintillations may be utilized to determine the number of α-particles being emitted by a known quantity of a radioactive substance. Since each α-particle emitted represents the disintegration of one atom, the method is

invaluable in determining the rate of atomic disintegration and, through it, the period, especially of the very long- or short-lived elements which are not subject to other more direct methods.

The range of α-particles in a given gas is inversely proportional to the pressure, which means that the number of molecular encounters necessary to exhaust its kinetic energy due to radioactive change is constant for a given gas. The reciprocal of the range in any gas is termed its *stopping power.* The total ionization in any gas produced by one α-particle is called its total ionization and when referred to air as a standard (air = 1) is called the *total specific ionization.* The molecular specific ionization is the ionization referred to air along equal lengths of path, i.e., through the same number of molecules of any gas. In the following table will be found data relative to ionization and stopping power.

TABLE I

STOPPING POWER AND IONIZATION (BY α-RAYS) OF DIFFERENT GASES ACCORDING TO BRAGG[1]

	$k \times 100$	$s \times 100$	$ks \times 100$
Air	100	100	100
H_2	100	24	23.3
N_2	96	98.9	94
O_2	113	106.4	109
CO	101.5	98.5	100
NO	—	—	128
CO_2	103	150.5	152
N_2O	105(99)	146	153
NH_3	90	—	81
CS_2	137	218	299
SO_2	103	—	201
He	—	20.1	21.1
Ar	—	95.1	124.5
Br	—	—	390
HBr	129	—	—
HI	129	—	—
HCl	129	—	—
CH_4	118	86	110
CH_4O	122	—	174
C_2H_2	126	112	140
C_2H_4	122	135	165
C_2H_6	130	151.4	197
C_5H_{12}	135	354.4	485
C_2H_6O	123	200	246
C_6H_6	129	333	430
CH_3I	133	258	343
C_2H_5I	128	312	400
$CHCl_3$	129	316	408
CCl_4	132	400	528
CH_3Br	132	203	275

Total Ionization (k); Stopping Power (s); and Molecular Ionization (ks).

[1] W. H. Bragg, Studies in Radioactivity, MacMillan, p. 65, 1912.

β-Particles: These are swift electrons which, like α-particles, originate in the nucleus of the atom. The mass of a stationary electron is 1/1834 that of the hydrogen atom or 0.898×10^{-27} g. The mass of β-particles whose velocity approaches that of light has been found to increase in conformity with the relativity theory.

$$m = m_0 \left[1 - \left(\frac{v}{c} \right)^2 \right]^{-1/2},$$

where m_0 is the stationary mass, m is the mass at velocity v, and c is the velocity of light. Some β-particles from RaC have the velocity equal to $0.998c$. From other sources, β-particles vary in initial velocity. They cease to ionize air below a velocity of $0.0063c$.

Owing to the small mass of an electron compared to a helium atom, β-particles have much less kinetic energy than α-particles. Consequently, they are much more easily deflected by magnetic and electrical fields, have a much smaller ionizing power, are more easily scattered and therefore pursue a more tortuous path in a gas. A β-particle of velocity $0.9c$ produces in air (N.T.P.) about 55 pairs of ions per 1 cm. of path or about 1/200 the ionization of an α-particle.

The high velocity of β-particles seems to be very unfavorable for the loss of energy through ionization. Consequently, β-particles are far more penetrating than α-particles and follow quite a different absorption law. While all α-particles from the same source traverse the same distance, called the range, in a given substance and produce ionization according to a specific law, β-particles do not all complete a path of the same length, but are successively stopped according to an exponential absorption law, i.e., in passing through successive equal layers of the same material the same fraction of those entering is stopped in each layer according to the equation

$$I = I_0 e^{-\mu d},$$

in which I_0 is the initial intensity of β-particles, I the intensity after passing thickness d in an absorbing medium with the absorption coefficient μ.

$$\mu = \frac{ln\ 2}{\mathrm{D}} = \frac{0.693\ \text{cm.}^{-1}}{\mathrm{D}}.$$

The half value layer D bears the same relation to μ as the half life period of radioactive elements does to θ the average life.

The following table shows the absorption coefficient in aluminum of β-particles from different sources. The higher the absorption coefficient the softer the β-particles.

γ-Rays: In γ-rays one has the most penetrating form of radioactive radiation. The doubt as to their nature which earlier existed has been dispelled; they are electromagnetic disturbances of the same nature as light, but of extremely short wave-length and correspondingly greater penetrating power. They are not deflected by magnetic or electric fields.

TABLE II

ABSORPTION COEFFICIENTS OF β-PARTICLES

Element	μ	D cm.$^{-1}$ Al
UX_1	510	1.36×10^{-3}
UX_2	14	4.8×10^{-2}
Ra	312	2.2×10^{-3}
RaB	13 : 78; 890	5.3×10^{-2}; 9×10^{-3}; 8×10^{-4}
RaC	13 : 53	5.1×10^{-2}; 1.4×10^{-2}
RaD	5500	1.2×10^{-4}
RaE	43	1.6×10^{-2}

The crystal lattice method, which has proved invaluable in the spectrum analysis of X-rays, may be extended to the softer γ-rays, but the harder rays are too short in wave-length for the crystal spacing to produce interference phenomena. The successive layers of atoms in the lattice act like a Rowland grating to produce interference and suppression of all rays except those of a given wave-length λ at a given angle of incidence (φ) with the plane of the crystal lattice, according to the relation

$$n\lambda = 2d \cdot \sin \varphi,$$

when n is a whole number 1, 2, 3, etc., and d is the lattice constant or the distance between the crystal planes, which, for rock salt, is 2.8×10^{-8} cm.

The law of absorption for a homogeneous bundle of γ-rays is exponential like that of β-particles, but the absorption coefficient μ is much smaller for γ-rays, and, consequently, the half layer D in a given material much greater. For example, D_{Pb} is 0.5 mm. for the most penetrating β-particles and 14 mm. for the hardest γ-rays.

As will be seen from the following table of μ for γ-rays from RaC in various substances, μ varies approximately directly with the density.

TABLE III

ABSORPTION COEFFICIENTS OF γ-RAYS[1]

Substance	μ_γ	μ_γ/Density
H	0.621	0.045
Pb	0.533	0.047
Cu	0.395	0.044
Fe	0.356	0.045
Sn	0.299	0.041
Zn	0.322	0.045
Al	0.126	0.047
S	0.091	0.046
H_2O	0.055	0.055
Air at 15°	4.64×10^{-5}	0.0378

The coefficients in aluminum of γ-rays from various elements are shown as follows:

[1] Hevesy and Paneth, Lehrb. d. Radioaktivität, Barth, Leipzig, p. 40, 1923.

TABLE IV

ABSORPTION COEFFICIENTS OF γ-RAYS IN ALUMINUM

Element	μ_γ	Element	μ_γ
RaB	230	Ra	354
	40		16.3
	0.51		0.27
RaC	0.40	$MsTh_2$	26
	0.115		0.116
	0.111		0.119
ThD	0.096	Io	1088
	0.0916		22.7
			0.408

The energy distribution among the various types is by no means equal. In the radium series, by far the greatest part of the γ-ray energy is emitted by RaC, in the thorium series $MsTh_{II}$ and ThC emit penetrating γ-radiation in quantities of the same approximate magnitude.

The ionization produced by γ-rays is largely due to the electrons set free with sufficient velocity to ionize gas molecules along their paths. The number of ions per second produced by the γ-radiation of RaC is approximately equal to that of β-radiation. Owing, however, to the much larger paths of the γ-rays, the ionization per cm. of path is much smaller than in the case of β-particles.

Secondary Rays: All three types of rays, α, β and γ, are capable of causing emission of secondary radiation from the molecules by which they are absorbed. The secondary radiation may be either electronic or electromagnetic in nature. The initial velocity of the secondary β-rays or electrons generated by γ-rays depends on the hardness of the γ-radiation and is limited by the quantum relation

$$eV = h\nu,$$

when ν is the γ-ray frequency and eV the maximum energy of the secondary electrons, but is independent of the nature of the matter in which the absorption takes place and of the intensity of primary γ-radiation. The number of secondary β-rays is proportional to the γ-ray intensity and increases with the atomic weight of the absorbent. When the primary γ-radiation falls on an absorbing screen, the secondary β-radiation emitted from the entering side is termed incident; its intensity increases with the screen thickness and for aluminum attains half value at 0.5 mm.; it also increases with the atomic weight of the screen material. The intensity of the secondary β-radiation emitted from the opposite side of the screen exceeds the incident secondary radiation in all substances except in lead. With increasing thickness of screen it increases to a maximum and this again falls off.

The production of secondary X- or γ-radiation by electrons is also according to the quantum relation just as in the converse process discussed above. Accordingly, 2500 volts would be required to supply the energy (eV) necessary to generate X-rays of $\lambda = 4.88 \times 10^{-8}$ cm. The softest γ-ray of RaB (λ

$= 1.365 \times 10^{-9}$ cm.) would require 89,000 volts, and the hardest γ-ray from RaC (λ not accurately known) would require a voltage of the order of 2,000,000 volts. The present X-ray technique is limited to about 350,000 volts which leaves the corresponding X-ray lacking the penetrating power of the hardest γ-rays by about 14 fold.

Secondary rays both of the β- and γ-ray type are also produced by α-radiation. The secondary β-particles are very soft, with only about four times the energy necessary to produce one pair of ions in air. The δ-rays which are emitted by all α-radiations are also slow electrons or very soft β-rays of secondary origin.

Recoil Atoms: When an α-particle is emitted from an atom of a radioactive element, according to the principle of action and reaction a recoil motion is imparted to the residue of the parent atom impelling it in the direction opposite to that taken by the α-particle. It becomes the recoil atom. If m and v be the mass and initial velocity of the α-particle and M and V those of the recoil atom, then by the principle of equal momentum $MV = mv$, from which

$$V = \left(\frac{m}{M}\right)v \qquad \text{and} \qquad \tfrac{1}{2}(MV^2) = \left(\frac{m}{M}\right)\tfrac{1}{2}(mv^2).$$

That is, both the velocity and kinetic energy of the recoil atom [1] is that fraction of the velocity and kinetic energy of the α-particle, represented by the ratio of the mass of the α-particle to the mass of the resulting recoil atom $\left(\frac{m}{M}\right)$, which, for the different cases arising, will have values between 1/50 and 1/60.

The recoil atoms from α-particles are swift enough to produce very intense ionization, though over a very limited range. The recoil atoms resulting from RaA have a range in air of about 0.14 mm. and of 0.83 mm. in hydrogen. This is about 1/350 of the range of the α-particles emitted, and since the energy of the recoil atoms is about 1/50 that of the α-particle, the rate of energy absorption must be about 7 times as great by recoil atoms as by α-particles. It has been found that the maximum ionization by recoil atoms is about 5 times as great as that of α-particles over the same path in air.

Owing to their lower velocities relative to those of α-particles, recoil atoms diminish in ionizing power with diminishing velocity over their whole paths, or, in other words, they exhibit only that final rapidly dropping part of the ionization curve shown for α-particles in their final stage when absorption and scattering are very rapid (see p. 1324).

Recoil atoms have, like α-particles, the property of activating some elements and of causing chemical reaction to ensue at ordinary temperature.[2] Those will be discussed in a later section.

[1] Meyer and Schweidler, Radioaktivität, Teubner, Leipzig, p. 261, 1916.

[2] Lind. *J. Am. Chem. Soc.*, **41**, 551, (1919).

TABLE V

INTERNATIONAL TABLE OF THE RADIOACTIVE ELEMENTS AND THEIR CONSTANTS, 1923[1]
(Series of Uranium and Radium)

Element	Symbol	Atomic Wt.	Atomic No.	Isotope	Half Period	Range cms. air 0° 760	Ions per $1\alpha \times 10^{-5}$	Rays	Velocity in terms of light	Absorption Coefficients μ_βAl	μ_γAl	μ_γPb
Uranium I	U_I	238	92	U	4.67×10^9 yrs.	2.37	1.16	α	0.0456	—	—	—
Uranium X_1	UX_1	234	90	Th	24.6 days	—	—	β	—	463	—	—
Uranium X_2	UX_2	234	91	Pa	1.15 min.	—	—	$\beta(\gamma)$	—	14.4	24; 0.7; 0.14	0.72
Uranium II	U_{II}	234	92	U	2×10^6 yrs.	2.75	1.27	α	0.0479	—	—	—
Ionium	Io	230	90	Th	6.9×10^4 yrs.	2.85	1.31	α	0.0485	—	—	—
Radium	Ra	226	88	Th$\times$	1690 yrs.	3.13	1.36	$\alpha(\beta + \gamma)$	α 0.0500; β 0.52; 0.65	312	354; 16; 0.27	—
Radon	Rn	222	86	Tn	3.85 days	3.94	1.55	α	0.0540	—	—	—
Radium A	RaA	218	84	Po	3.0 min.	4.50	1.70	α	0.0565	—	—	—
Radium B	RaB	214	82	Pb	26.8 min.	—	—	$\beta(\gamma)$	0.36; 0.41; 0.63; 0.70; 0.74	13.1; 80	230; 40; 0.51	—
Radium C	RaC	214	83	Bi	19.5 min.	—	—	99.97% β and γ	0.786; 0.862; 0.949; 0.957	13.2; 53	0.115	0.50
Radium C′	RaC′	214	84	Po	10^{-6} sec.	6.57	2.20	α	0.0641	—	—	—
Radium D	RaD	210	82	Pb	16.5 yrs.	—	—	(β and γ)	0.33; 0.39	5500	45; 0.99	—
Radium E	RaE	210	83	Bi	5.0 days	—	—	β	—	43.3	—	—
Radium F	RaF	210	84	Po	136 days	3.58	1.50	$\alpha(\gamma)$	0.0523	—	585	—
Radium G (U–Pb)	RaG	206	82	Pb	Infinite	—	—	—	—	—	—	—
Radium C	RaC	214	83	Bi		?	1.47	0.03% α	—	—	—	—
Radium C″	RaC″	210	81	Tl		—	—	β	—	—	—	—

[1] *J. Am. Chem Soc.*, **45**, 872 (1923).

Recoil atoms from β-particles have velocities of the same order of magnitude as gas molecules at ordinary temperatures. Ionizing properties have not been observed, but, occasionally, recoil from β-rays has been observed with sufficient energy to remove the parent atom from the active surface. The energy of recoil from α-particles is far greater and has been utilized to separate members of the radioactive disintegration series from their parent members.

The Uranium Series: Uranium is the parent member of the best known of the three radioactive families. The members of this series and some of their most important radioactive and other properties are shown in the preceding table.

Where branching occurs in the series it is indicated by the percentage shown for the first two members resulting from the two limbs of the branch. For example, UX_1 disintegrates into UX_2 to the extent of 99.65 per cent, and to UZ to the extent of 0.35 per cent. Similarly, UY is a 3 per cent branch from U_{II}. UY is probably the parent of protactinium, the initial member of the actinium family (see the actinium series).

Before taking up the individual members of the uranium series, some of the general principles that can be deduced by inspection of the table will be considered. Of course, many of the data given in the table are calculated by means of these principles, and thus the table was constructed by a process the reverse of the one that will now be followed.

α-Ray Changes: Whenever an α-ray change is observed it will be found that the atomic weight is diminished by four units. This follows from the fact that a helium atom of atomic mass four is removed from each atom. This principle has been verified experimentally in a number of ways. In passing down the series from uranium (238) to radium, three α-ray members U_I, U_{II} and Io are involved; hence one would predict a drop in atomic weight of 3×4 units, or radium should have the atomic weight 226 which has been verified by the very accurate work of Honigschmid.[1] Again, there are 5 α-ray members between radium and RaG, leading one to expect an atomic weight of 206 for RaG, which has been verified by Richards,[2] Hönigschmid [3] and others. Finally the entire span from Th (232) to ThD involves six α-radiators and ThD has been found by Hönigschmid and Horovitz [4] to have an atomic weight of approximately 208.

Moreover, the volume of pure radon has been found to be about 0.6 mm.^{3} per curie, which is the volume to be expected from the number of α-particles emitted and the Avogadro number (total number of molecules in a gram-mol. $= 6.06 \times 10^{23}$).

It may also be observed that the emission of one α-particle leads to a new atom with an atomic number lower than that of the parent atom by two units, which follows directly from the definition of the atomic number as the net positive charge on the nucleus and the fact that an α-particle removes two

[1] *Sitzb. Akad. Wiss. Wien*, **120**, 1617 (1911).

[2] T. W. Richards and P. Putzeys, *J. Am. Chem. Soc.*, **45**, 2954 (1923).

[3] O. Hönigschmid and St. Horovitz, *Sitzb. Akad. Wiss. Wien*, **123**, 2407 (1914).

[4] *Sitzb. Akad. Wiss. Wien*, **123**, 2407 (1914).

positive unit charges. Similarly, the removal of a β-particle from the nucleus increases the net positive charge and hence the atomic number by one unit. It follows that, whenever the succession of changes in any series is such that an α-radiator is preceded by, followed by, or lies between two β-radiators, the net result is an element with an atomic weight four units lower, but having the same atomic number as the original element at the head of the changes. Since it has been shown that isotopes have the same atomic number, one should expect the initial and final members of such a series of changes to be isotopic. This is verified in a number of cases in the various families, for example, by the sequence $U_I \xrightarrow{\alpha} UX_1 \xrightarrow{\beta} UX_2 \xrightarrow{\beta} U_{II}$. A number of highly important relationships arise in the periodic system from the principles just stated, but their full consideration will be more advantageously approached after the other two radioactive families have been presented.

The Thorium Series: Like the uranium series this series has at its head an element known before the discovery of its radioactive properties. It has many points of similarity to the uranium series. Its members emit the same types of radiation with the same general characteristics. One and only one gaseous member occurs, thoron, which is the parent of a sequence of members showing striking common properties with the corresponding members in the uranium series. The branching which takes place at ThC giving 35 per cent of ThC'' and 65 per cent of ThC' is a much more evenly balanced branching than is found in the uranium series. Other important differences are the occurrence of a marked γ-radiator ahead of thoron, and the brief life of the latter. Also $MsTh_1$ which corresponds most closely to Ra has a life so much shorter that it cannot be collected in sufficiently large quantities to enable the direct determination of its atomic weight. The characteristics of the series are given in Table VI.

The Actinium Series: This series has long been known to be genetically related to the uranium series. The exact position of the branching has been the object of much research and speculation. While it is still in doubt, the origin suggested is at present regarded as the most likely one, namely, a 3 per cent α-ray branching to UY from which protactinium is formed by a β-ray change. The actinium series is presented in the accompanying table (Table VII).

What Constitutes a Radioactive Series? The fact that the actinium series is a branch of only 3 per cent from the uranium series has been pointed out. It has also been seen that other branches, even of much higher percentage, are not designated as independent series. One of the distinguishing characteristics of a series has always appeared to be the occurrence of one and of only one gaseous member. As will be shown later, these gaseous members belong to the rare gas group like argon, krypton and xenon. A study of the section on the displacement law (p. 1347) will disclose the probability that one and only one gaseous member should be included in a series. In other words, the radioactive elements extend over only about one and a half octaves in the periodic system. On going lower in atomic weight, the stable elements are encountered, on going higher one reaches a region of instability apparently so great that

TABLE VI[1]

INTERNATIONAL TABLE OF THE RADIOACTIVE ELEMENTS AND THEIR CONSTANTS, 1923
(Series of Thorium)

Element	Symbol	Atomic Wt.	Atomic No.	Isotope	Half Period	Range cms. air 0° 760	Ions per $1\alpha \times 10^{-5}$	Rays	Velocity in terms of light	Absorption Coefficients μ_βAl	Absorption Coefficients μ_γAl	Absorption Coefficients μ_γPb
Thorium	Th	232	90	Th	1.31×10^{10} yrs.	2.58	1.23	α	0.0469	—	—	—
Mesothorium 1	$MsTh_1$	228	88	Ra	6.7 yrs.	—	—	—	—	—	—	—
Mesothorium 2	$MsTh_2$	228	89	Ac	6.2 hrs.	—	—	β and γ	0.37; 0.39; 0.43; 0.50; 0.57; 0.60; 0.66 and > 0.70	20.2 to 38.5	36; 0.116	0.62
Radiothorium	RdTh	228	90	Th	2.02 yrs.	3.67	1.53	$\alpha(\beta)$	α 0.0527; 0.47; 0.51	—	—	—
Thorium X	ThX	224	88	Ra	3.64 days	4.08	1.61	α	0.0546	—	—	—
Thoron	Tn	220	86	Rn	54 sec.	4.74	1.78	α	0.0574	—	—	—
Thorium A	ThA	216	84	Po	0.14 sec.	5.40	1.92	α	0.0600	—	—	—
Thorium B	ThB	212	82	Pb	10.6 hrs.	—	—	β and γ	0.63; 0.72	110	160; 32; 0.36	—
Thorium C	ThC	212	83	Bi	60 min.	—	—	65% β	(C + C″) 0.29; 0.36; 0.93 to 0.95	14.4	—	—
Thorium C′	ThC′	212	84	Po	10^{-11} sec.	8.16	2.54	α	0.0688	—	—	—
Thorium D (Th–Pb)	ThD	208	82	Pb	Infinite	—	—	—	—	—	—	—
Thorium C	ThC	212	83	Bi	—	4.55 ?4.69	1.71	35% α	0.0572	—	—	—
Thorium C″	ThC″	208	81	Tl	3.1 min.	—	—	β and γ	(See ThC)	21.6	0.096	0.46

[1] *J. Am. Chem. Soc.*, **45**, 873 (1923).

TABLE VII[1]

INTERNATIONAL TABLE OF THE RADIOACTIVE ELEMENTS AND THEIR CONSTANTS, 1923
(Series of Actinium)

Element	Symbol	Atomic Wt.	Atomic No.	Isotope	Half Period	Range cms. air 0° 760	Ions per $1\alpha \times 10^{-5}$	Rays	Velocity in terms of light	Absorption Coefficients μ_βAl	Absorption Coefficients μ_γAl	Absorption Coefficients μ_γPb
Uranium Y	UY	?	90	Th	1.04 days	—	—	β	—	About 300	—	—
Protoactinium	Pa	?	91	Pa	1.2×10^4 yrs.	3.314	1.44	α	0.0510	—	—	—
Actinium	Ac	?	89	Ac	20 yrs.	—	—	—	—	—	—	—
Radioactinium	RdAc	?	90	Th	19.5 days	4.36	1.69	$\alpha(\beta)$	α 0.0559; β 0.38, 0.43; 0.49; 0.53; 0.60; 0.67; 0.73	About 170	25; 0.19	—
Actinium X	AcX	?	88	Ra	11.4 days	4.17	1.61	α	0.0550	—	—	—
Actinon	An	?	86	Rn	3.9 sec.	5.40	1.95	α	0.0600	—	—	—
Actinium A	AcA	?	84	Po	2.0×10^3 sec.	6.16	2.12	α	0.0627	—	—	—
Actinium B	AcB	?	82	Pb	36.1 min.	—	—	(β and γ)	—	Very large	120; 31; 0.45	—
Actinium C	AcC	?	83	Bi	2.15 min.	5.12	1.88	α	0.0589	—	—	—
Actinium C″	AcC″	?	81	Ti	4.71 min.	—	2.1 ?	β and γ	—	28.5	0.198	1.2 to 1.8

[1] *J. Am. Chem. Soc.*, **45**, 872 (1923).

the elements, if they ever existed, no longer are found, or at least have not yet been discovered.

The general characteristics of the genetic series of elements and of their principal radioactive properties may be learned from Tables V, VI and VII; the properties and separation of the individual radioactive elements may now be considered.

Nomenclature: The nomenclature of separate elements, while greatly improved by unification, is not yet on a strictly scientific basis. Several different principles have been followed. The most consistent has been that of attaching the first letters of the alphabet to the numbers below the gaseous member as RaA, B, etc., and, similarly, ThA, etc., and AcA, etc. Another principle has been that of attaching to the parent of the series prefixes like meso- and radio- to distinguish certain members above the gaseous members, or to affix the final letters of the alphabet like X, Y and Z. Isotopy has been indicated in some cases like $\overline{U}_1$ and $\overline{U}_2$. The several principles may lead to more than one name for the same element; for example, RaG is also called U-Pb. Individual names like polonium (RaF) and ionium have also been adopted for some of the early discoveries. The term *emanation* was adopted for the gaseous members before their material nature was recognized. While very generally accepted, the disadvantages are serious; in English at least, the layman has always confused the terms *emanation* and *radiation*, leading to unfortunate popular conceptions, such as the possibility of accumulating and storing the radiations. On the other hand, separate terms like *niton* for RaEm (Rn) has the serious disadvantage of losing the family name and of requiring too many new terms if all the radioactive elements were given such names. Hence the names *radon, thoron* and *actinon* seem most satisfactory and have been adopted for the gaseous members of the three families.

Uranium: This element consists of at least two isotopes U_1 and U_2, though the latter, on account of its shorter life, constitutes only 0.04 per cent of the equilibrium mixture. U_2 cannot be separated from U_1 but may be obtained by growth from UX_1 which has been separated chemically from the mixture. The experimental value 238.18 for the atomic weight of U has been determined with the greatest care, and, although it has brought it much closer to 238.0, which would correspond to 226.0 for U_1, than the old value 238.5, the discrepancy with theory is serious enough to suggest it may contain a third unknown isotope of higher atomic weight. This has suggested a different possibility for the origin of actinium from that shown in the actinium series, with the hypothetical U isotope as its parent.

The very long periods of decay of U_I and U_{II} preclude the direct observation of their values; they have been calculated from the rate of emission of α-particles and from the Geiger-Nuttall relation. Either the black oxide (U_3O_8) or the uranyl nitrate ($UO_2(NO_3)_2.6H_2O$) is usually employed as an α-ray standard in radioactive measurements. The old system of reporting even high values of activity in terms of the uranium equivalent has been abandoned in favor of the International Radium Standard (see p. 1337).

$U\overline{X}_1$ is an isotope of Th and would therefore be similarly separated (see Ionium, below).

$U\overline{X}_2$ is an isotope of Pa and may be obtained from solutions of $U\overline{X}_1$ either by electrolytic separation or by precipitation together with tantalum oxide.

UY and UZ receive their names from their occurrence in uranium salts. Their weak activity compared with other β-radiators makes it evident they are not members of the main $\overline{U}$ series. The exact method of their genesis is not clear but the evidence points toward UY as the parent of PrAc and hence of the Ac series.

Ionium: This possesses especial interest as the parent of radium and also as an α-radiator of suitable life period to be of practical interest if it could be obtained in a pure state. This latter has not been possible on account of its being an isotope of thorium so that the purest ionium yet obtainable was estimated by atomic weight determination to contain only 30 per cent Io, though the two atomic weights are so close together that the greatest experimental accuracy leaves the calculated purity in considerable doubt.

Radium: This is the radioactive element of the greatest theoretical and practical interest. Its life is sufficiently long for it to accumulate in quantities which have rendered its separation feasible in quantities readily handled by ordinary chemical methods. Its atomic weight has been determined with great accuracy. Its spectrum has also been determined. It is the next higher homologue above barium in the periodic system to which it has great similarity in chemical properties. The corresponding radium and barium salts are isotropic. Owing to their chemical similarity, radium and barium are not easily separated by reactions involving fractional precipitation or solution. So far reaching is this inseparability under ordinary circumstances that radium and barium have been referred to as "pseudo-isotopes." Radium and barium are readily separated by the fractional crystallization of their chlorides and, more readily, of their bromides.

Radium is isotopic with $MsTh_1$ and $Th\overline{X}$, but, owing to the small quantity of Th in the principal ores of $\overline{U}$, radium is not usually contaminated with $MsTh_1$ to a serious extent. Like the corresponding barium salts, $RaCl_2\ 2H_2O$ and $RaBr_2.2H_2O$ are readily soluble in water, which should be acidulated with HCl or HBr to prevent precipitation by carbon dioxide or as basic salts that might be formed in the oxidizing atmosphere produced by the action of α-rays on water. Such solutions are extensively employed for the collection of radon for therapeutic use.

The two most commonly prepared insoluble salts of radium are the carbonate ($RaCO_3$) and sulfate ($RaSO_4$). The former is soluble in HCl or HBr.

When the salts of radium are sealed up in small volumes, care must be taken to remove the last traces of water (even of crystallization), otherwise the decomposition of water by α-rays will lead to the liberation of hydrogen (and oxygen ?),[1] which, in the limited space, produces dangerous pressures in the glass tube containers.

[1] Oxygen may be wholly utilized in forming oxyhalide salts, leaving only hydrogen free. This is surmised from the fact that the equilibrium $2H_2 + O_2 \rightleftharpoons (2H_2O)$ under α-radiation

Measurement of Radium: This is accomplished either by the α-ray solid method, the radon method, or the γ-ray method, depending on circumstances.

The γ-ray method is used for the comparison of the larger quantities of radium (> 1 mg.) in a fairly concentrated state (> 1 per cent purity). Either an electroscope or an electrometer may be used. All α- and β-radiation is screened out by a lead screen $\frac{1}{8}$ to $\frac{1}{4}$ inch thick. Of course, the γ-radiation compared is from RaC, and hence the preparation must have been sealed at least one month for the RaC to accumulate to equilibrium quantity. Otherwise, the time of accumulation must be accurately known and a suitable correction be applied to obtain the equilibrium value. *International radium standards* have been prepared by recrystallizing radium chloride until pure and especially free from barium chloride, as indicated by very careful atomic weight determinations. Weighed quantities of the pure radium chloride were sealed up in glass tubes and compared by their γ-radiations. Those independently prepared by Mme. Curie and by Hönigschmid were found to be in good agreement for the γ-radiation from equal weights. Hence 1 gram has been adopted as the unit quantity of radium element.

Occurrence and Recovery of Radium: Radium occurs in the great majority of uranium minerals in the equilibrium ratio of 1 part of radium to 3,000,000 parts of uranium by weight. The only exceptions are: (1) Ores of too recent origin for radioactive equilibrium to have been reached. (2) Some uranium ores of secondary origin of rather loose structure are subject to removal of part of the radium content by leaching, leaving the Ra : U ratio below normal. Correspondingly, some natural waters are found to contain measurable quantities of radium in solution.

The recovery of radium from uranium ores may be accomplished in one of two general methods: (1) Attack by an acid like hydrochloric or nitric acids which take radium into solution: after filtration radium is precipitated together with barium as sulfate. (2) The ore is attacked directly with sulfuric acid, converting the radium and barium into sulfate which must be removed from the insoluble ore residue by some kind of mechanical concentration. These two types of treatment are subject to various modifications. The result of the acid leach is sometimes more effective if sulfates be converted to carbonate by a previous carbonation, hot or cold, or sometimes by fusion, followed by a water wash to remove sulfates, before attacking the radium-barium carbonate with hydrochloric acid.

In all processes the radium at some stage is precipitated together with barium as sulfate. The proportion of $RaSO_4$ to $BaSO_4$ first precipitated varies, but is of the order 1 to 1,000,000 or less. If the ore has not this proportion of barium, it must be added in the leach or just before precipitation, to take advantage of the pseudo-isotopic property of barium toward radium, to insure good recovery. For the same reason, a soluble barium salt is added to a radium solution to "protect" the radium from precipitation by small accidental quantities of precipitant, thus preserving its full "emanating power."

has been found to lie far toward H_2O formation, and yet high pressures are known to be produced.

The co-precipitation of radium and barium presents some highly interesting features. It seems anomalous that radium should be precipitated together with barium at a concentration far below that corresponding to the solubility of pure radium sulphate (about 1/100 that of $BaSO_4$). This action is exactly that to be expected if radium and barium were truly isotopic, but they have, of course, atomic numbers widely different, and can readily be separated by fractional crystallization of the halides. Moreover, since they are not isotopic, one would expect the theoretically unstable condition established by the co-precipitation to revert to equilibrium by the return of radium into solution. Such is not the case. On the other hand, the degree of co-precipitation is not so rigid as with true isotopes. The behavior of isotopes in similar reactions will be discussed later in the section on the radio-elements as chemical indicators.

The Chemical Properties of Radium: The properties of the element are those to be expected from its position in the periodic system. For example, it may be predicted from the relative solubilities of $CaSO_4$, $SrSO_4$ and $BaSO_4$ that $RaSO_4$ should have a solubility less than that of $BaSO_4$ by about 100 fold, which has been found to be the case.[1] Similarly, from the solubility of $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ it may be predicted that $Ra(OH)_2$ should be even more soluble[2] than $Ba(OH)_2$. This has been confirmed and made use of in their separation in strongly alkaline solutions at low temperature.

In general, it should be noted that the radioactive properties of an element are exhibited only at the moment of transition to another. Looked at statistically, only that fraction of the atoms undergoing radioactive change within a given interval of time is responsible for the radiation and for the other radioactive manifestations; the remaining atoms, either before or after change, have only the properties of ordinary chemical elements.

Radon: This is the highest homologue of the noble gas series. Owing to its property of diffusing from solids and solutions containing radium and apparently of producing radioactive properties in the objects with which it comes in contact, it was given the name radium *emanation*. As already pointed out, this term as well as others proposed should be abandoned for the name *radon* proposed by the International Committee of Chemical Elements. The critical temperature of radon is + 105°, its boiling point is − 62°, its freezing point − 71°. The solubility in water diminishes with the temperature; it also obeys Henry's law. The partition coefficient between air and water is at 0°, 0.510; at 10°, 0.350; at 16°, 0.3; at 20°, 0.255; at 100°, 0.107. Salts in solution lower the solubility; the coefficient in 1 molar salt solution at ordinary temperature is 0.16; between blood and air at body temperature is 0.42.[3] Most organic liquids dissolve radon to a greater degree than does water.

The percentage loss of radon from solids has been termed "emanating power" of the solid in question. Dry radium salts usually lose by diffusion

[1] Lind, Underwood and Whittemore, *J. Am. Chem. Soc.*, **40**, 465 (1918).

[2] R. K. Strong, *J. Am. Chem. Soc.*, **43**, 442 (1921).

[3] Mache and Suess,, *Wien. Ber.*, **121**, 171 (1912).

only about 10–15 per cent of their equilibrium quantity of radon. Wetting or heating materially raises the proportion liberated. Compact ores like pitchblende, even when finely ground, lose only a few (3–8) per cent; carnotite loses much more (16–50 per cent). Raising the temperature of dry salts, even to 1000° C. or higher, has not proved an efficient method of de-emanating; treatment by solution or fusion is necessary.

The quantity of radon in equilibrium with 1 gram of radium is termed 1 *curie;* it has the volume 0.63 mm.^{3} and weighs 6×10^{-6} mmg. The curie [1] is subdivided into milli-, micro-, and milli-micro-curies.

The absolute *purification* of radon in order to determine its true volume is of great scientific interest but very difficult to accomplish. Less rigid purification is sufficient for many scientific and for therapeutic purposes. The usual practice is to maintain a solution of radium (chloride or bromide) in acid solutions with high protective barium to prevent precipitation. From this solution the radon is collected under vacuum and separated from the decomposition products of the solution by suitable chemical treatment. The principal impurities are hydrogen and oxygen from the decomposition of water by α-rays, of which hydrogen is in excess owing to the formation of oxyhalides and H_2O_2 in solution, but principally due to hydrogen from the decomposition of the halide acid, the halogen having been retained by mercury in the collecting system. Other impurities are carbon dioxide by oxidation of stop-cock grease, organic gases from its decomposition by α-rays, and helium. The latter can be removed only by freezing the radon by liquid air and pumping off the residual gas.

Besides its convenience as a source of γ-radiation, radon may be employed as a source of α-rays by mixing it in the system to be radiated; it may also be confined in small glass capillaries or bulbs with walls a few microns thick which allow the passage of α-particles with an absorption equivalent to about 1 cm. of air per 6 microns of glass.

The rate of decay of radon when separated from its parent, radium, or of its production in its presence may be obtained from the following table for $e^{-\lambda t}$. It will be noticed that radon accumulates from 0 to practically 100 per cent in about 1 month, and attains half volume in 3 days and 21 hours.

Short-lived Active Deposits: The first three members below radon, RaA, RaB and RaC, are all rather short-lived. Consequently, radon attains equilibrium in about 4 hours with all three. Since they are solids, they are deposited on the surface of any object with which they come into contact and thus produce the phenomenon originally called "induced radioactivity," now termed "active deposit."

On account of its strong γ-activity, RaC is the most important member. This γ-radiation furnishes the most convenient means of measuring RaC and,

[1] A concentration unit based on the electrical discharging power of radon has also been employed. 1 Mache unit = 3.6×10^{-10} curie/liter. Essentially, the Mache unit is now a wholly secondary one, unscientific in definition, impractical to determine, and should be abandoned.

TABLE VIII

DECAY OF RADIUM EXAMINATION ACCORDING TO L. KOLOWRAT

Time		Quantity Remaining $e^{-\lambda t}$	Δ 0 00	Time		Quantity Remaining $e^{-\lambda t}$	Δ 0 00	Time		Quantity Remaining $e^{-\lambda t}$	Δ 0 00
Days	Hrs			Days	Hrs			Days	Hrs		
	0	1 00000		1	11	0 76913		4	3	0 47592	
			375				575				353
	0 5	0 99625		1	12	0 76338		4	6	0.46533	
			372				570				345
	1	0 99253		1	13	0 75768		4	9	0.45498	
			742				567				337
	2	0 98511		1	14	0 75201		4	12	0 44486	
			736				562				330
	3	0 97775		1	15	0 74639		4	15	0 43496	
			730				557				323
	4	0 97045		1	16	0 74082		4	18	0.42528	
			726				554				315
	5	0 96319		1	17	0 73528		4	21	0 41582	
			719				549				308
	6	0 95600		1	18	0 72979		5	0	0 40657	
			715				545				3004
	7	0 94885		1	19	0 72434		5	4	0 39155	
			709				542				2915
	8	0 94176		1	20	0 71892		5	8	0 38289	
			703				537				2829
	9	0 93473		1	21	0 71355		5	12	0 37158	
			699				533				2745
	10	0.92774		1	22	0 70822		5	16	0 36059	
			693				529				2664
	11	0 92081		1	23	0 70293		5	20	0 34994	
			688				525				2585
	12	0 91393		2	0	0 69768		6	0	0 33960	
			683				522				2509
	13	0 90710		2	1	0 69246		6	4	0 32956	
			678				517				2435
	14	0 90032		2	2	0 68729		6	8	0 31982	
			672				514				2363
	15	0 89360		2	3	0 68215		6	12	0 31037	
			668				509				2293
	16	0 88692		2	4	0 67706		6	16	0 30019	
			663				504				2225
	17	0 88029		2	6	0 66698		6	20	0 29229	
			657				496				2160
	18	0 87372		2	8	0 65705		7	0	0 28365	
			653				489				2096
	19	0 86719		2	10	0 64726		7	4	0 27527	
			648				482				2034
	20	0 86071		2	12	0 63763		7	8	0 26714	
			643				475				1974
	21	0 85428		2	14	0 62813		7	12	0 25924	
			639				468				1915
	22	0 84789		2	16	0 61878		7	16	0 25158	
			633				461				1859
	23	0 84156		2	18	0 60957		7	20	0 24414	
			628				454				1804
1	0	0 83527		2	20	0 60050		8	0	0 23693	
			624				447				1751
1	1	0 82903		2	22	0 59156		8	4	0 22993	
			620				440				1699
1	2	0 82283		3	0	0 58275		8	8	0 22313	
			614				432				1649
1	3	0 81669		3	3	0 56978		8	12	0 21654	
			611				422				1600
1	4	0 81058		3	6	0 55711		8	16	0 21014	
			605				413				1553
1	5	0 80453		3	9	0 54471		8	20	0 20393	
			601				404				1507
1	6	0 79852		3	12	0 53259		9	0	0 19790	
			597				395				1462
1	7	0 79255		3	15	0 52074		9	4	0 19205	
			592				386				1419
1	8	0 78663		3	18	0 50916		9	8	0 18637	
			588				378				1377
1	9	0 78075		3	21	0 49783		9	12	0 18087	
			583				369				1326
1	10	0 77492		4	0	0 48675		9	18	0 17291	
			579				361				1268

TABLE VIII—(*Continued*)

Time		Quantity Remaining $e^{-\lambda t}$	Δ 0 00	Time		Quantity Remaining $e^{-\lambda t}$	Δ 0 00	Time		Quantity Remaining $e^{-\lambda t}$	Δ 0 00
Days	Hrs			Days	Hrs			Days	Hrs		
10	0	0 16530	1212	14	16	0 07136	0519	21	12	0 02086	01496
10	6	0 15803	1159	15	0	0 06721	0489	22	0	0 01906	01367
10	12	0 15107	1108	15	8	0 06329	0461	22	12	0 01742	01250
10	18	0 14442	1059	15	16	0 05961	0434	23	0	0 01592	01142
11	0	0 13807	1013	16	0	0 05613	0409	23	12	0 01455	01044
11	6	0 13199	0968	16	8	0 05287	0385	24	0	0 01330	00954
11	12	0 12619	0925	16	16	0 04979	0362	24	12	0 01216	00872
11	18	0 12063	0885	17	0	0 04689	0341	25	0	0 01111	00797
12	0	0 11533	0846	17	8	0 04416	0321	25	12	0 01015	00728
12	6	0 11025	0809	17	16	0 04159	0303	26	0	0 00928	00637
12	12	0 10540	0773	18	0	0 03916	02809	27	0	0.00775	00532
12	18	0 10076	0739	18	12	0 03579	02567	28	0	0 00647	00441
13	0	0 09633	0701	19	0	0 03271	02346	29	0	0 00541	00371
13	8	0 09072	0660	19	12	0 02990	02144	30	0	0.00452	—
13	16	0 08543	0622	20	0	0 02732	01960	40	0	0 000747	—
14	0	0 08046	0586	20	12	0 02497	01791	50	0	0 000123	—
..	8	0 07577	0552	21	0	0 02282	01637	∞		0 00000	

through it, both radium and radon. The γ-radiation of RaC is also that utilized for therapeutic purposes.

Active deposits may be most conveniently collected from the gas, either with or without the aid of an electric field. The former is the more efficient method. A metallic wire, disk or plate on which it is desired to collect active deposit is charged negatively to about 300 volts. Owing to the residual *positive* charge of the active deposit, it is collected on the cathode, though never with 100 per cent efficiency. By making the time of collection long or short, the long- or short-lived members are relatively favored. Subsequent separation is usually desirable and this is accomplished in a number of ways. (1) To remove RaA, advantage may be taken of its short life, so that after 15 or 20 minutes have elapsed only RaB and RaC remain; they may be separated either electrolytically or by their difference in volatility. At 800°, 75 per cent of RaB and only 20 per cent of RaC are volatilized.

In order to effect chemical or electrolytic separation, the active deposit is dissolved from the wire or foil in dilute acid and the usual method for the separation of bismuth (isotopic with RaC) and lead (isotopic with RaB) is applied. At a cathode potential of not over -0.5 volt and a current density of 0.4 milliampere per cm.^{2}, pure RaC is deposited. More simply, the C-

members may be deposited from weakly acid solution on nickel foil. Retention of RaB in solution is promoted by the addition of a Pb salt, though this is not permissible if pure RaB is desired.

RaA is isotopic with RaC′ and polonium which have no isotope among the common elements.

RaB is a lead isotope. It emits β- and γ-radiation which, though much less penetrating than that of RaC, is sufficiently intense to cause confusion in making γ-ray comparisons of radium preparations not in equilibrium (hence containing different proportions of RaB) with a standard in equilibrium, unless sufficient lead screening is used ($\frac{1}{4}$ inch) to stop γ-rays from RaB.

RaC is a bismuth isotope. It shows the property of branching, 99.97 per cent going by β- and γ-radiation to RaC′ and 0.03 per cent by α-radiation to RaC″.

RaC′, isotopic with polonium, is the parent of RaD. It emits the most penetrating set of α-rays in the U-Ra series.

RaC″ is a thallium isotope. It emits β-rays and probably produces RaD, though there is some doubt on this point.

RaD is a lead isotope, frequently referred to as radio-lead. Its half period is not very definitely known (16–20 years). Being the longest-lived member between radium and RaG, it controls the rate of formation of RaF (polonium). The result is that when a short but intense exposure to radon has produced (in an electroscope or in a room) an intense α-radiation, which dies out rapidly with the decay of the short-lived members, a longer-lived α-radiation will be developed slowly and reach its maximum intensity years later, as controlled by the long-lived RaD.

English lead contains such quantities of RaD that it cannot be used for making electroscopes until RaD has had time to decay. Consequently old cathedral roofing 300 years or more old is preferred. American lead is free of RaD and can be used at once.

RaE is a bismuth isotope which cannot be accumulated in visible or weighable quantities on account of its rather short half-period, 4.85 days.

RaF has no isotopic member among common non-radioactive elements. Its other isotopes are still shorter-lived, and hence the properties of this family of isotopes must be studied by means of polonium, which has a half-period of 136 days. It is quite similar in chemical properties to the analogues bismuth and tellurium. It has been shown by Paneth [1] to be capable of forming a hydride. In neutral or weakly acid solution, polonium exists in the colloidal state. Polonium possesses scientific interest as a pure α-radiator, owing to the fact that when it is separated from preceding elements there are no succeeding ones to produce a contaminating β- and γ-radiation. This condition is not met so favorably elsewhere among the radioactive elements.

RaG is the end member of the U-Ra series. It is isotopic with lead, and has been found to have the theoretical atomic weight 206. This, together with the fact that it has been found to accumulate in uranium minerals progressively

[1] *Ber.*, 51, 1704–28 (1918).

with their geological ages, leads to the conclusion that it is a stable element. The estimation of geological age by the accumulation of lead or of helium will be discussed in a later section.

Actinium Series: Progress in the elucidation of the origin of the actinium family has been somewhat slow. From its first discovery it was known to be genetically related to the uranium series, even before the existence of protactinium or of $U\overline{Y}$ had been suspected. The present status of this problem is that UY seems to be the head of the branch, because its radiation (or "atomic flux" (see p. 1334)) corresponds in quantity to the known radiation of other members of the actinium series, and secondly because it fits the displacement law. But the parentage of UY is still quite problematical. Besides the hypothesis already proposed that U_{II} is its parent, there are two other possibilities, U_1 and a possible third unknown uranium isotope U_3. Without a knowledge of this parentage there is no starting point for the estimation of atomic weights in the actinium series and the perplexity is increased by the fact that no member of the family has been obtained in sufficient quantity for an atomic weight determination, the best opportunity for which seems to lie with protactinium; this would also settle the question of parentage.

Protactinium has the properties of a higher homologue of tantalum, and its complete separation from tantalum is consequently difficult.

Actinium is a higher homologue of lanthanum. Its preparation in a pure state would be of interest in that it has no common isotopes and hence is the most abundant representative of a new type of element; but its rather short life seems to preclude such a realization.

Radio-actinium is isotopic with thorium, ionium and radio-thorium. Actinium X is isotopic with radium, mesothorium I and thorium X. Both RdAc and AcX are α-radiators. In the observed ranges of their α-particles, 4.36 and 4.17 cms. respectively, they violate the general rule that the shorter-lived element emits α-particles of the greater range.

Actinon, like thoron and radon, is a heavy member of the rare gas series. Owing to its very short life (half-period of 3.92 secs.), it cannot be accumulated in quantity. The succeeding members of this series are also very short-lived, the longest being AcB, a lead isotope with a half-period of 36.1 minutes. AcA and AcC′ are isotopes of Po, ThA and ThC′ and like Po emit α-rays. AcC is a bismuth isotope and AcC″ a thallium isotope.

Members of the Thorium Series: Thorium is the parent element of a third radioactive family that has no genetic relationship to the other two.[1] This is apparent from the wide divergence of thorium and uranium content of different minerals which are found with a content all the way from uranium minerals with little or no thorium to thorium minerals almost without uranium. On the whole, the former is more common (i.e., uranium without thorium); most thorium minerals do contain more or less uranium, but there is no reason to believe the association to be a genetic one.

[1] This has been questioned by Hirsch, *Wien. Ber.*, **131**, 551 (1922).

For the ordinary properties of thorium and of its compounds one may consult the chemical reference books. The element is but little known, but has recently had a limited application as the target in X-ray tubes. The two commonest compounds are the oxide (ThO_2) and the nitrate ($Th(NO_3)_4$). The usual source of thorium is monazite sand which is found containing up to 8 per cent ThO_2. The principal use of thoria is in the preparation of gas mantles. Thorium minerals are relatively more abundant than those of uranium, but owing to absence of any member of long life, it has no products which accumulate in chemically measurable quantities; even from the radioactive standpoint its members are of less interest than those of the radium family.

Meso-thorium is isotopic with radium, and may, as immediate parent of the radioactively important members of the thorium series, be regarded in a very general way as comparable with radium. However, its much shorter half-life (6.7 years) places serious limitations on its usefulness in many directions. $MsTh_1$ itself emits no measurable rays: A weak β-ray emission is inferred on genetic grounds but, as immediate parent of $MsTh_2$, it rapidly acquires a penetrating β- and γ-radiation, which can be utilized therapeutically like that of RaC. A complication arises from the additional penetrating γ-radiation from ThC''. The following table shows how the γ-radiation changes during the first ten years of the life of a MsTh preparation.

TABLE IX

CHANGE OF THE γ-RAY ACTIVITY OF MESO-THORIUM WITH TIME[1]

Years	$MsTh_1$—$MsTh_2$	ThC''	Total
1	1.000	0.000	1.000
2	0.881	0.489	1.370
3	0.777	0.781	1.558
4	0.685	0.935	1.620
5	0.604	1.000	1.604
6	0.531	1.007	1.538
7	0.469	0.973	1.442
8	0.413	0.921	1.334
9	0.364	0.855	1.219
10	0.321	0.786	1.107

[1] Hevesy and Paneth, Lehr d. Radioaktivität, Barth, Leipzig, p. 163, 1923.

It will be seen that the maximum γ-radiation is not attained until between the fourth and fifth years. The ultimate rate of decay becomes that of $MsTh_1$ itself (T = 6.7 yrs.). This is so much shorter than that of radium as to constitute a serious drawback in acquiring $MsTh_1$ for therapeutic use instead of radium. This difficulty is in part compensated by the lower cost (on a basis of equal γ-radiation) of meso-thorium on account of its production as a by-product in the gas mantle manufacture. But, at best, after the lapse of 25–30

years one would have but little radiation left [1] from an initial investment in meso-thorium, whereas radium would have diminished but little more than 1 per cent. Another disadvantage in the therapeutic use of meso-thorium lies in the short life of thoron which makes it impossible to collect it and use it like radon.

On the other hand, meso-thorium preparations may very suitably be used to replace radium in the so-called luminous zinc sulfide paints. The phosphorescent zinc sulphide itself as well as some of the objects on which it is used has a very limited life; therefore, MsTh is much more suitable.[2]

Since $MsTh_1$ is isotopic with radium, the same methods of chemical separation may be employed. In fact, since meso-thorium is usually accompanied by radium, it is more convenient to control the process and recoveries by means of radium than of meso-thorium determinations.[3]

Since high-grade radium preparations are measured by means of their γ-radiation, it is important to know whether any of this radiation is contributed by meso-thorium. Such contamination would be disclosed in the course of time by a too rapid rate of γ-ray decay, or in the earlier part of the life of the preparation by a rise (see Table IX). Meyer and Hess [4] have described a method of estimation based on the difference in penetrating power of the γ-rays from radium and from meso-thorium, which can be carried out without opening the containers. More accurate is the determination of the radium by the emanation method, which involves, however, opening the container and putting at least part of the salt into solution.

Meso-thorium$_2$ is isotopic with actinium. As already stated, it contributes the penetrating β- and γ-radiation to its parent $MsTh_1$ with which it gets into equilibrium in a few days. Neither of these emits α-rays.

Radio-thorium is isotopic with thorium and ionium. Its α-radiation is its most characteristic property. It may be separated from $MsTh_1$ preparations by precipitation with ammonia.

Thorium X also emits α-rays and is isotopic with radium. Its half period of 3.64 days is very close to that of radon, and makes it a very suitable object of radioactive examination.

Thoron is isotopic with radon, emits α-rays, but differs greatly in having a half-period of less than a minute. When radium is determined by the radon method, thoron, if present, is allowed to decay, by delaying the introduction of the gases into the ionization chamber. In the usual procedure where three or four hours are permitted to elapse before measuring the activity of radon, thoron itself would have decayed, but would have left behind a much longer-lived active deposit, that would not be permissible in the ionization chamber.

Thorium A, an isotope of polonium, has a half period of only 0.14 sec.

[1] Most preparations of MsTh from monazite contain about 18–20 per cent of Ra on the γ-ray basis.

[2] R. B. Moore, *Bull. Inst. Min. Met. Eng.*, Aug. (1918).

[3] H. Schlundt, *U. S. Bureau of Mines Tech. Paper*, 265, p. 18 (1922).

[4] *Sitzb. Akad. Wien*, **123**, 1443 (1914).

Thorium B is one of the lead isotopes. It emits only β- and γ-radiation but is immediately succeeded by a series of fairly short-lived α-radiators, and its presence or quantity may be determined by α-ray methods. By mixing with a lead salt, the isotopic relation may be employed to determine lead indirectly through ThB in very minute quantity. This method has been used in studying the assimilation of lead salts in plants, the distribution of lead in other organisms, the solubility of very slightly soluble lead salts, etc.[1] The method is limited by the fairly short life of ThB. When the time elapsing between making the isotopic mixture and the measurement is long, a correspondingly higher quantity of ThB must be added initially. A time correction is avoided by making the final comparison against a sample of the original mixture, which must have undergone the same change in activity. This application of the inseparability of isotopes for analytical purposes is fully discussed in a later section.

Thorium C is isotopic with bismuth. Like RaC and AcC it is the parent of an α-radiator, thorium C′ isotopic with Po and of a β- and γ-radiator, thorium C″ isotopic with thallium. The α-particles from ThC′ have a range in air of 8.6 cms., the longest in either of the three radioactive families.

Potassium and Rubidium: Among the ordinary elements, besides uranium and thorium, potassium and rubidium have long been known to emit a weak β-radiation. The small number of β-rays emitted in comparison with any of the β-radiators of the three radioactive series makes it improbable that potassium and rubidium themselves are responsible for the radiation. Two theories have been advanced: (1) that a higher homologue of the alkali series is radioactive and that it is associated to some extent through its "pseudo-isotopism" with the lower homologues potassium and rubidium. This theory receives some support through the fact that the missing element of atomic number 87 may belong to the alkali series and presumably would be radioactive. On the other hand, cæsium does not possess radioactivity,[2] although, as the highest known homologue, it would be expected to be most similar to the yet higher radioactive member and hence should show the association in enhanced degree. (2) The other theory is that the radioactivity of potassium and rubidium are due to one of their isotopes present in but limited quantity. Rubidium has isotopes of atomic weights 85 and 87. This explanation is supported by the fact that the absorption of the β-radiation in the cases of potassium and rubidium does not indicate that they are identical, as should be the case if due to the same higher radioactive homologue. But the theory of radioactive isotopes of potassium and rubidium leaves unexplained how radioactivity could be possessed by elements of such low atomic weight. The product of a β-emission would have an atomic number one unit higher which, in the case of potassium, would be a calcium isotope and in the case of rubidium a strontium isotope. Further light may be thrown on the subject by the examination of the atomic weights of calcium and strontium from various sources.

[1] Hevesy, *Biochem. J.*, **17**, 439 (1923).

[2] This has been questioned by Zwaardemaker, *Proc. Acad. Sci. Amsterdam*, **26**, 575–81 (1923), who finds it also to have a very weak β-radiation.

Radioactive Isotopes: The general conception of isotopism arose, as is well known, from the study of the radioactive elements. Two principal considerations led inescapably to this conclusion. The number of new elements disclosed by radioactivity was too great to be accommodated in the previously known periodic system. The "atomic rooming-house" became so overcrowded that it was necessary either to alter the entire structure or else to accommodate more than one member in the same room. This latter alternative, which would previously have been regarded as absolutely opposed to the conception of the elements, received the necessary support through the observation of the chemical and physical inseparability of certain elements, which from their radioactive properties were not only known to be entirely separate elements, but which could actually be separated and obtained in their pure states by radioactive methods, utilizing differences of origin or different rates of radioactive decay or of generation.

As has already been shown (Chapter I), isotopism was soon proved to be characteristic of many of the non-radioactive elements. In fact, the results of Thomson, Aston, Dempster and others have proved that isotopy is the rule rather than the exception among all the elements. Through the skill of Harkins[1] and his co-workers, of Brönsted and Hevesy[2] and of others, the partial separation of ordinary isotopes has been accomplished.

TABLE X

GROUPS OF RADIOACTIVE ISOTOPES

Periodic System	Elements	
	Period VI	Period VII
Group II	....	.. Ra, $MsTh_1$, AcX, ThX
Group III	Tl, AcC″, ThC″, RaC″	Ac, $MsTh_2$
Group IV	Pb, RaG, ThD, AcD, RaD, ThB, Ac, RaB	Th, Io, RdTh, UX_1, RdAc, UY
Group V	Bi, RaE, ThC, Ra, AcC	Pa, UX_2, UZ
Group VI	Po, RaA, ThA, AcA, AcC′, RaC′, ThC′	U_I, U_{II}
Group VIII	Rn, Tn, An	

The Displacement Laws: Not only has the periodic system been proved to be capable of giving a logical place to all the elements and of explaining the remarkable similarities of those that occupy the same place, but the order of sequence of the radioactive elements with reference to the radiations emitted furnishes a wonderful genetic picture of the radioactive part of the periodic system. The two displacement laws are remarkably simple and comprehensive. The first states that when an α-particle is emitted, the atom loses

[1] Harkins and Madorsky, *Nature*, **111**, 148 (1923). *J. Am. Chem. Soc.*, **45**, 591 (1923)
[2] *Nature*, **106**, 144 (1920); **107**, 619 (1921); **109**, 780 (1922).

a mass of four units and the net positive charge of the nucleus (atomic number) loses two units. Hence, the number of electrons outside the nucleus is reduced by two, the element loses valency by two units, and the resulting atom will have a place in the periodic system two places to the left of the parent element. The second law states that when a β-particle is emitted, the nucleus becomes more positive by one unit; hence, the valency is increased by one unit, and the element moves one place to the right in the periodic system. It is seen, therefore, that the result of a β-ray change is opposite in direction but of half value as compared with that of an α-ray change. Hence an α-ray emission followed by two successive β-ray emissions will result in an element of the same nuclear charge but of different atomic weights from the original, and therefore an isotope of lower atomic mass has resulted. The same would result from any other order involving two β's and one α, like β–β–α or β–α–β. The accompanying diagram (Fig. 2) shows the relations fully. By starting at uranium or

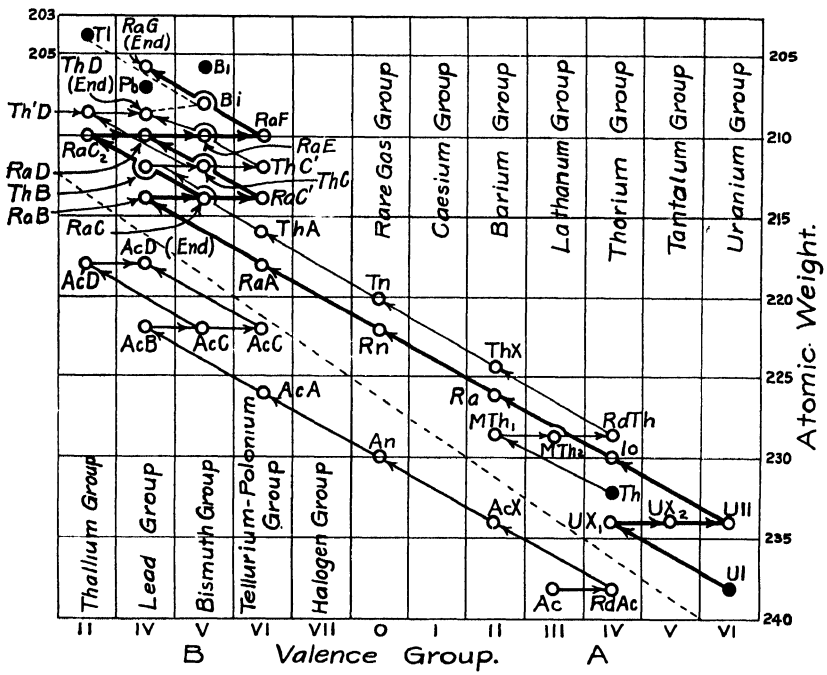
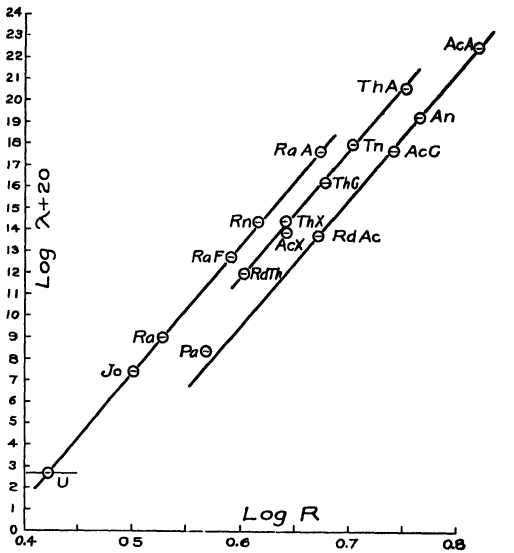


FIG. 2. Radioactive Disintegration Series

thorium one may trace the entire relation between radiation, genetics and the periodic systems of the radioactive elements. An extraordinary picture of the evolution of elements is presented, which suggests many future possibilities with reference to the evolution of the ordinary elements that are too visionary at present to be more than mentioned.

The Geiger-Nuttall Relation: A purely empirical relation was discovered by Geiger and Nuttall [1] which has been of great practical service. They observed that the more rapid the rate of decay of an α-radiator the greater the range of the α-rays. If $\log \lambda$ (where λ is the decay constant) be plotted against $\log R$ (the range), a straight line results. As will be seen from Fig. 3, the lines have the same slope for all three of the radioactive series. The equation is: $\log \lambda = A + B \log R_0$, where A is a constant characteristic of each series, with the value -37.7 for the uranium series; B has the same value for all of the series -53.9; R_0 is the air range at 0° and 760 cms. As has been stated (p. 1343), AcX is an exception.



Relation between Range(R) and Decay Constant(λ) of α-Radiators

FIG. 3

This empirical rule has been of great use in calculating the immeasurably short period of the long range α-radiators. It has not yet been possible to elucidate the theoretical significance of the relation; evidently, it may be expected to have a profound relation to the structure of the nucleus and to the instability of the nucleus as illustrated by α-ray emission.

Radioactive Elements as Indicators: The inseparability of isotopes first made itself evident as a disadvantage in the impossibility of separating elements like radium and meso-thorium or thorium and ionium. But, conversely, it may be utilized to advantage in non-isotopic separations by adding a large quantity of one of the isotopic groups to be held back or separated.

Paneth, Hevesy [2] and others have also shown that isotopy may be utilized for analytical purposes. If, for example, it is desired to determine lead in minute quantities not subject to ordinary analytical methods, one may add RaD or the still more sensitive and correspondingly less stable ThB in a known ratio (empirical in terms of radioactive units) to the lead. Since this ratio will not be changed by any chemical or ordinary physical processes, minute quantities of lead may be determined indirectly by using the extremely sensitive radioactive methods for the radioactive isotope, and multiplying the result by the chosen ratio. The method has been shown to be applicable to the

[1] *Phil. Mag.*, **22**, 613 (1911); **23**, 439 (1912).

[2] Hevesy and Paneth, Lehrb. d. Radioaktivität, Chap. 15, Barth, Leipzig, 1923.

determination of the solubility of slightly soluble salts, of the distribution of lead or other suitable elements in plants or animals, or of other physical distribution. It has been found that free interchange takes place between lead ions in solution, but not between lead ions and lead in an organic radicle. Numerous applications will suggest themselves, such as the indirect determination of the course of meso-thorium in an extraction process by means of radium determination by the emanation method.[1]

Inseparability, even, of the limited degree exhibited by substances which are only "pseudo-isotopic" like radium and barium, can be advantageously applied. Some radium production plants follow the course of radium through the process by means of barium determinations.

In the case of gases, no isotopic relations are necessary, in using radioactive indicators. For example, radon at low concentration in air or other gases may be used in studies of air circulation, and of the diffusion of gases through fabrics, diaphragms or other systems.

The Artificial Disruption of Atoms: The knowledge that the heavier atoms are being spontaneously disrupted and changed into others in nature has led to an increased interest in the artificial disruption of atoms. This interest has been enhanced by the theory that the nuclei of all atoms are composed of the nuclei of helium and of hydrogen.

So far, attempts to effect the disruption of atoms artificially have not been successful except those of Rutherford employing high-speed α-particles. In other words, we have found no agent powerful enough to disrupt the nucleus except one arising from the natural disruption of another (radioactive) nucleus.

It is further notable that Rutherford has been able to disrupt only the light atoms (at. wt. < 32) which belong either to the $4n + 2$ or $4n + 3$ series.[2] Of the elements with atomic weight less than 32, he has succeeded by means of α-ray bombardment in knocking swift hydrogen atoms from boron, nitrogen, fluorine, sodium, aluminum and phosphorus.

The efficiency of the disruption is extremely low. Less than 1 α-particle in 100,000 strikes the atom in such a way as to eject a swift hydrogen atom. This is explained in part by the minute dimensions of the bombarded nucleus and of the α-particle (He nucleus) so that the probability of a head-on encounter is very small. Moreover, the positive charge of the nucleus repels the approach of the positive α-particle. This may explain why it is only the lighter atoms (of small nuclear charge) which are disrupted.

The evidence of the disruption consists in the detection by means of scintillations produced on a zinc sulfide screen of H-particles at a distance beyond the range of initial α-particles. This precludes the detection of any H-particles that might have a shorter range. The method also gives no information as to the nature of the residual atom resulting from the disruption.

The fact that only atoms of the $4n + 2$ or $4n + 3$ type are disrupted is interpreted to mean that the nuclei composed solely of He nuclei are very

[1] Schlundt, *Tech. Paper* 265, *U. S. Bureau of Mines.*

[2] Kirsch and Pettersson, *Nature*, **113**, 603 (1924), report cases of $4n$ elements also being disrupted.

stable; further, that the additional 2 or 3 H's are probably satellites of the $4n$ nucleus and hence more readily removed. Rutherford explains, on this basis, how some swift hydrogen atoms are ejected counter to the direction of bombardment, by assuming that the H satellite upon being struck describes a partial orbit about the nucleus before flying away.

The relative instability of $4n + 2$ or $4n + 3$ nuclei is in accord with the remarkable deductions of Harkins made several years previously from the relative abundance of the elements.

Rutherford's earlier claim to have knocked swift He atoms from nitrogen has not been supported by his later researches.[1]

It appears highly significant that Rutherford[2] finds that the sum of the kinetic energy of all atoms involved in the disruption is greater after the collision than before. Evidently, this contribution of additional energy comes from the intra-atomic energy of the atom disrupted. The excess in some cases is as much as 40 per cent of the initial energy of the bombarding α-particle.

Chemical and Physical Effects of the Radiations: Among the purely physical effects of the rays may be considered the heat evolution, and the ionization. Many purely chemical effects are also produced by the action of the rays on the substances through which they pass. Another class of effects such as luminescence or phosphorescence, coloring, etc., cannot with certainty be called either physical or chemical, but are nevertheless important and will be considered here.

The heat evolved from radioactive elements may be accounted for by the absorption of the radiations. The ionization alone is not sufficient to account for the total kinetic energy. Resonance probably accounts for the balance.

Coloring by Radiation: The rays from radium have the property of imparting color to many transparent or semi-transparent substances like salts, glasses, minerals, etc. The colors vary in hue, even for the same mineral, probably due to a variation in something present as an impurity. The same kinds of variations are produced as are found in nature, and it has been suggested that the colors of colored minerals in nature are due to radiation received from the earth. While this may be true in some instances, it can by no means be maintained as a general truth. The stability of the colors also shows the greatest variation, from those which fade in the dark, in diffuse light, in direct sunlight, in ultra-violet light, to those permanent over long periods of time in strong sunlight. Heat is found to discharge the colors in all cases, though the temperature and time of heating vary widely for different substances. In general, those substances most readily colored are most easily decolorized and *vice versa*.

Usually the color can be produced either by α- or by β- and γ-radiation, but, in the case of diamond, it is found that only non-penetrating (presumably α-) radiation produces color, which in diamond is invariably green. Rock salt is colored an amber yellow; topaz, amber brown; kunzite, light green; quartz

[1] E. Rutherford, *J. Chem. Soc.*, **121**, 400 (1922).

[2] E. Rutherford, *Phil. Mag.*, **44**, 432 (1922).

varies from no color to smoky brown or black; amethystine color was produced only after decoloring amethyst quartz by heat and then radiating; sapphire varies from golden yellow to green, blue green and gray; ruby and emerald are not colored; aquamarine appears absolutely resistant to coloring.

The theory of the color is not well understood. Its discussion is deferred to the following section where it is considered in connection with the luminescent effects.

Luminescent Effects: High-grade radium salts are continuously luminescent in the dark to the rested eye. When the salt has recently been heated to a red glow for a short time, the luminescence is greatly enhanced and is much bluer. The enhanced blue luminescence is only temporary and disappears in a few days.

In the same way, radioactive radiation of sufficient intensity renders certain other substances luminous. In general, they are the same kind of substances that are colored by the radiation, but there are exceptions in both directions: namely, substances like rock salt that become decolorized without showing any luminous effects, and some, like calcites, which show both fluorescence, phosphorescence and marked thermo-phosphorescence but little or no coloring.

Among the substances that fluoresce or phosphoresce, the greatest variety of behavior is exhibited in the color of the light, the duration of phosphorescence, the response to different kinds of radiation, the effect of impurities, etc. Some substances like phosphorescent zinc sulfide (Sidot blende) are especially sensitive to α-rays; others, like willemite (a silicate of zinc) and barium platinocyanide, respond more readily to β- and γ-radiation. Most diamonds respond to α-radiations but not at all or only weakly to penetrating radiation.

The influence of small quantities of certain impurities is very evident in many cases and may be inferred in others. This statement applies to the luminescent effects in many substances, apparently to the coloring of some, and even to tribo-luminescence. For example, it has been shown that very pure zinc sulfide does not respond to α-radiation and is not photo-phosphorescent. Different calcites [1] show variations in all the luminescent effects which cannot be readily attributed to anything but difference in impurities present. Most zincblende (ZnS) is not triboluminescent, but certain varieties containing manganese and iron are highly so. The variations in color displayed by different glasses and by different specimens of some minerals point to the influence of variation of constituents or of very dilute impurities, in some cases too small to be detected.

It has frequently been suggested that there is a close connection between the coloring of substances by radiation, the emission of light during decolorization, and certain electronic phenomena.

Meyer and Przibram [2] have shown that the photoelectric effects are enhanced in kunzite and fluorspar by radiation. Roentgen [3] points out that

[1] W. P. Headden, *Am. J. Sci.*, **5**, 314 (1922); **6**, 247 (1923).
[2] *Sitzb. Akad. Wien*, **123**, 653 (1914).
[3] *Ann. Physik*, **64**, 1 (1921).

the electrical conductivity of sodium chloride crystals is increased by X-radiation and especially by light rays after X-radiation. Lenard [1] and his co-workers have made numerous contributions which strengthen the idea that electrical phenomena are an essential part in if not the cause of the color and luminescence.

Meyer and Przibram have proposed a theory according to which electrons liberated by the radiation serve to neutralize the metallic ions of the crystal lattice, leaving the neutral atoms free to coagulate into clusters of colloidal size which produce color. Heating produces the reverse reactions and the electrons in returning to their original positions or associations cause luminosity. This theory is supported by the observation that decolorization and thermo-phosphorescence usually appear to be coincident (though violet-colored glass is a marked exception) and the fact that synthetic borates of different metals take the same colors as the colloidal solutions of organic salts of the corresponding metals.

A less complicated theory [2] assumes displacement of electrons into new positions which produce color, their return to the original positions producing light. By assuming that there may be more than one set of electronic positions, one could account for the independence of discharge of color and of thermo-phosphorescence as in the case of glass.

It has been recently shown [3] that the total amount of light emitted from equal portions of glass exposed to the same penetrating radiation is constant and independent of the temperature or rate of heating. The temperature coefficient for 10° is not far below 2, which would also indicate the chemical nature of the reaction. A slow loss of thermo-phosphorescent power, even at ordinary temperature, is shown by glass retained for several years after radiation before being heated; the thermo-phosphorescence is then much lower. In other words, the reversion is taking place slowly even at room temperature, and may be accompanied by the same character of light emission as at higher temperatures, but with an intensity too low for it to be detected.

Among the physical effects of radiation, one of the most important is the continuous heat evolution due to the absorption of the rays by the material through which they pass. Meyer and Hess [4] have determined that one gram of radium in equilibrium with Rn, RaA, RaB and RaC evolves 132 small gram calories per hour. Rutherford [5] calculated the following distribution: α-particles (and recoil atoms) from Ra, 25.1 cal.; from Rn, 28.6; from RaA, 30.5; from RaC, 39.4; total, 123.6; β-rays from RaC, 4.3; γ-rays from RaC, 6.5; grand total for radium in equilibrium, 134.4, in good agreement with the results of Meyer and Hess obtained under conditions where only about 15 per cent of the γ-radiation was absorbed.

[1] *Ann. Physik*, (4) **38**, 553 (1922).

[2] Lind and Bardwell, *J. Franklin Inst.*, **196**, 387 (1923).

[3] R. E. Nyswander and S. C. Lind, *Phys. Rev.*, **23**, 296 (1924).

[4] *Sitzb. Akad. Wien*, **121**, 603 (1912).

[5] Rutherford, E., "Radioactive Substances," p. 581 (1913).

The Chemical Effects of Radioactive Radiations: All three types of rays are capable of bringing about chemical reaction. Since the α-rays are by far the most energetic, carrying about 95 per cent of the total energy radiated by radium and its decay products, they are the most effective in producing chemical reaction.

Reactions of very varied character are brought about, those that proceed with free energy decrease as in the combination of oxygen with hydrogen, with carbon monoxide or with methane, or of hydrogen with chlorine or with bromine. Reactions occurring with free energy increase are also brought about, as in the decomposition of water and of ice, of ammonia, hydrogen chloride and bromide, hydrogen sulfide and nitrous oxide. Polymerization as in the formation of ozone from oxygen is also effected by α-radiation.

The most convenient radioactive agent in the production of chemical reaction is the gas radon. It may be used directly by mixing it with the gas or liquid to be acted on or it may be confined in minute glass bulbs with walls thin enough to transmit α-rays.

By comparing the ionization produced with the number of molecules caused to react, it has been found for a large number of reactions in gaseous and liquid systems that the M/N ratio is in the neighborhood of unity (M being the number of molecules reacting and N being the number of pairs of ions). A probable interpretation of this fact is that the ions are chemically active and constitute intermediate products in the reaction. The next step in many reactions appears to be the formation of an *addition complex* between the positive ion and one or two neutral molecules. This may be illustrated in the decomposition of carbon monoxide by α-rays as follows:

$$\begin{aligned} CO + (\alpha) &= CO^+ + (-), \\ CO^+ + CO &= (CO)_2{}^+, \\ (CO)_2{}^+ + (-) &= CO_2 + C, \end{aligned}$$

showing that two carbon monoxide molecules react for 1 ion. In this particular reaction the free electron acts merely to re-establish electrical neutrality. This appears natural since carbon monoxide has no affinity for free electrons [1] and hence could not form negative ions. In gases containing oxygen, however, which is a good electron trap, negative (O_2^-) ions are formed which are also chemically active and thus *double* the effectiveness of the reaction. In the synthesis of water from hydrogen and oxygen,[2] for example, the M/N ratio is 4 instead of 2.

The effectiveness of a single α-particle in producing chemical reaction evidently will depend on the quantity of ionization it produces in the system. In a liquid system, where its energy is entirely absorbed, it produces its maximum of ionization and of chemical reaction. In a gaseous system of limited dimensions, the ionization will depend on the path traversed in the gas, and

[1] L. B. Loeb, *Phil. Mag.*, **43**, 229 (1922); H. B. Wahlin, *Phys. Rev.*, **20**, 267 (1922).

[2] Lind, "Chemical Effects of α-Particles and Electrons," A. C. S. Monograph No. 2, p. 117 (1921).

on the pressure and stopping power of the latter. In case inert gases are present, they have no effect except to absorb part of the α-ray energy; the partial pressures of the reactant gases will determine, through their stopping powers, the proportion of the ionization that is effective. For spheres from 1 to 6 cms. in diameter filled with hydrogen and oxygen in the molecular ratio 2 : 1 and acted on by radon, it has been shown that the rate of the reaction is proportional to the diameter of the vessel or to the average path of the α-rays. For non-stoichiometric mixtures those richer in oxygen show a faster rate than in the normal mixture, while those richer in hydrogen show a slower rate. This is explained by the difference in stopping power or of relative ionization of hydrogen and oxygen.

The energy utilization is, in most reactions, only a few per cent of the total kinetic energy of the α-particles. This will be more fully discussed later.

The relative effect of β-radiation appears to be in the same ratio to ionization as in the α-ray reactions. Kailan [1] has shown in a large number of reactions in liquid systems that the M/N ratios are not far from unity. Owing to the weak absorption of γ-rays it is not convenient to produce quantitatively measurable chemical reactions with γ-rays alone.

The recoil atoms from α-rays have also been shown to produce combination of hydrogen and oxygen with the same M/N ratio as do α-particles. In small spheres (diameter less than 1 cm.) and at low pressures, their effect even exceeds that of the α-particles since the latter lose most of their energy in the glass walls.

Radiographic Effects: All three types of rays produce radiographic effects which are undoubtedly chemical in nature. The effect of the penetrating rays from uranium on the photographic plate was the means of the discovery of radioactivity. The effects are analogous to those produced by light. The photographic method of examining the radioactivity has the advantage that, by prolonged exposure, it has a cumulative effect which enables the detection and location of very weak sources, if they can be brought near the plate.

It has been shown that each grain of the silver salt that is struck by a single α-particle is rendered subject to development. The tracks of α-particles may be studied by means of the photographic plate; those which just graze the surface of the plate trace a track which has been identified with the range of α-particles in material of the density of gelatine.

Relation of the Radiochemical and Photochemical Effects: Strictly speaking, the term radiochemistry should include the chemistry of all kinds of radiation from light to corpuscular emissions which have the general characteristics of true radiation. For convenience, however, the radioactive chemical effects will here be referred to as *radiochemical* to distinguish them from the photochemical effects.

The principal difference appears in the non-selective action of α- and, to a less degree, of β-rays. α-particles may be thought of as piercing their way through a large number of molecules, removing an electron from each one

[1] *Z. physik. Chem.*, **95**, 215 (1920); **98**, 474 (1921).

encountered, leaving behind a number of chemically activated electrically charged ions. Ionization is universally produced in gases traversed by α-particles, according to principles which have already been discussed. No reciprocal or resonance effect is in evidence. On the other hand, one finds selectivity or resonance the most marked characteristic of photo-chemical effects. In the radiochemical effects, it is probable that activation is the result of ionization, though it is possible that some additional activation results from resonance or the shift of electrons to new energy levels without ionization. In the photochemical effects, ionization is usually not a factor; most probably resonance (the production of new Bohr states) accounts for the activity, though the possibility of a molecular splitting into free atoms may not be disregarded.

The Einstein photochemical equivalence law states that the primary activation is due to the absorption of at least 1 $h\nu$ per molecule of radiant energy of frequency ν. One may, therefore, speak of an $M/h\nu$ ratio in photochemistry, just as of the M/N ratio in the radiochemical effects. The two seem to have much in common. In both, the ideal case is represented by one in which the ratio is near unity. The departures of the $M/h\nu$ ratio are much more numerous and more exaggerated than of the M/N ratios. In the radiochemical effects, no case has yet been encountered except that of the hydrogen-chlorine combination, which exceeds unity by more than 6 fold, which can be explained by complex formation without a chain hypothesis. In the reaction between hydrogen and chlorine, Taylor[1] has shown the ratio $\frac{M_{HCL}}{N}$ to be 4–6 $\times 10^3$, while in the photochemical reaction $M_{HCL}/h\nu$ is about 1×10^6. These large deviations from unity have proved rather baffling. Nernst's chain hypothesis (p. 1226) is the one which is most favored. In photochemistry, many other cases are known which do not lend themselves so readily to a similar explanation.

Evidence from photochemical, radiochemical and electronically produced reactions seems conclusive that activated molecules, by whatever means activated, react with other unactivated molecules and thus enhance the reaction ratio a few fold. It is not yet evident, however, that the actual activated intermediates are the same even for the same reaction when they are produced by different agencies. As possibilities, one must consider ions, free atoms, and molecules with electrons in the various resonance states. The array of possibilities and the present paucity of experimental material leave much room for doubt, but the rapid progress being made in many directions lends much hope of an early solution of many of the most perplexing problems in radio- and photochemistry.

A low degree of energy utilization is characteristic of the radiochemical reactions as well as of photochemical ones. In many cases the utilization does not exceed 2 per cent. In photochemical reaction this was explained by Warburg on the assumption of a primary splitting into atoms which would

[1] H. S. Taylor, *J. Am. Chem. Soc.*, **37**, 24 (1915); **38**, 280 (1916).

require much more energy than would be represented by the net result of the reaction after their recombination to form new molecules. In the radiochemical reactions it has been pointed out by Lind[1] that assumption of the ionization theory of activation involves a low energy utilization since the quantity of energy necessary to ionize exceeds, by at least ten fold, that obtained from the chemical effect even in cases of the most vigorous reactions.

Radioactivity in Geology: The discovery of the presence of radioactive materials in the earth has given many new footholds for geological speculation and calculation. The extreme sensitiveness of the radioactive methods of measurement has enabled one to determine the quantity of members of both the radium and the thorium families present in the earth's crust. Besides the concentrated occurrences in the form of uranium and thorium ores, all soil, rocks and natural waters have been found to contain measurable quantities of both. It is quite remarkable that radium is found to be present both in acid and basic eruptive rocks and in sedimentaries in a proportion that varies only within the narrow limits $1\text{–}4 \times 10^{-12}$ gram of Ra per 1 g. of rock. Exceptions are known, but in by far the greater number of all kinds of rock the radium content falls within those limits. In general, the eruptives have a higher content than the sedimentaries; the basic eruptives have a lower content than the acid ones. The average radium content of the earth's crust, after allowance for the difference in character of the rocks composing it, has been estimated to be about 2×10^{-12} g. per gram, which corresponds to a uranium content 6×10^{-6} g. per gram. The average thorium content is somewhat higher, but of the same order of magnitude, about $1\text{–}2 \times 10^{-5}$ g. Th per gram. While these quantities do not appear large at first sight, they are sufficient, if distributed in the same concentration through the whole earth, to produce heat at a rate more than 100 fold that at which it is known to be radiated from the earth. Hence, the earth would be gradually warming up instead of cooling. Looked at in another way, with an outer shell about 16 km. thick, with a uranium and thorium concentration equal to those found at the earth's surface, a heat balance will be maintained. Various theories have been proposed by geologists seeking to avoid these conclusions, but they cannot be said to have attained their object. J. Joly[2] has recently elaborated a theory of cycles of successive periods of heating to the melting of the crust, rapid cooling to solidification, thickening of the crust to a maximum and so forth. These cycles are based on the theory of isostasy and the known radioactivity.

The data of radioactivity have also been used to calculate the age of minerals and, from such data, the age of the earth itself. In general, four different methods have been employed.

(*a*) In a mineral too young for radioactive equilibrium to have been thoroughly established with all the members of the family, the ratio found may be used to calculate the age of the formation. For example, when a Ra/U

[1] *Trans Am. Electrochem. Soc.*, **24**, 339 (1913).

[2] *Phil. Mag.*, **45**, 1167–88; **46**, 170–6 (1923).

ratio is found $< 3.4 \times 10^{-7}$, and there is no reason to believe leaching of radium has taken place, the ratio could be employed to estimate the age. This method is limited in application to very recent formations.

(*b*) A more general method is the determination of the accumulation of lead in a primary uranium mineral. This method has the advantage over (*a*) that, the older the mineral, the more accurate becomes the determination through the Pb/U, since the lead as a terminal member continues to increase. The method has the disadvantage that one is not always certain that some lead was not originally present with the uranium which would make the age appear too great. This can be settled only by an accurate atomic weight determination. It is also possible that the lead content may be too low, either by leaching or by leak of the gaseous emanation from the mineral. In dense minerals, like pitchblende, the loss of emanation is slight. The secondary disturbance, even of pitchblende, by leaching, may, however, become very large. Hönigschmid and Birckenbach [1] and Richards and Putzeys [2] have shown that the lead composing the secondary minerals of the Katanga deposit in the Belgium Congo is nevertheless primary uranium lead since it has the atomic weight 206, and must have been produced long before from some primary uranium mineral, probably pitchblende.

Another difficulty of the lead accumulation method is the fact that the value arrived at for the age of the same formations by the Pb/U ratio is 3–4 times greater than that from the Pb/Th ratio. While the former value was preferred for some time on account of doubt as to the absolute stability of ThD, the latest evidence points toward greater reliability for the shorter periods calculated from the Pb/Th values, which also are in better accord with the calculations from denudation. The discrepancy remains unexplained, but Joly [3] has recently proposed a most interesting theory that a third U isotope, now no longer existent, contributed the other $\frac{3}{4}$ of U-Pb by its more rapid decay.

(*c*) Besides the terminal member lead, another stable element results from radioactive change, namely, helium. It has the advantage in the uranium series of furnishing 8 and in the Th series 6 atoms of helium per 1 atom of lead. On the other hand, it has the disadvantage in being a light gas which is quite likely to diffuse away from the parent mineral. Indeed, if we accept the radioactive origin of all helium, the large total quantities found in natural gases makes evident its diffusion on a great scale. In general, the helium method has given values several fold lower than the lead methods.

(*d*) The *pleochroic haloes* that are found in certain micas have been identified as the radiographic coloring developed through geological ages by the α-radiation from a minute particle of radioactive material. Joly has succeeded in finding haloes at various stages of development and has concluded that rough age estimates can be made by means of their study. While it hardly seems possible that they will ever present a means of age estimation of accuracy

[1] *Ber.*, **56**, 1837 (1923).
[2] *J. Am. Chem. Soc.*, **45**, 2954 (1923).
[3] *Scientific Monthly*, **16**, 205 (Feb. 1923).

comparable with the other methods, they are nevertheless objects of the greatest interest in themselves. If we can accept the estimate that some of them contain such minute radioactive centers that only 80 α-particles per year are emitted, they evidently afford the most sensitive means we have of detecting matter. It is also of great interest that these minute spheres maintain their exact theoretical diameter through geological ages and hence show there is an absolute non-diffusibility of one solid in another.

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