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TORONTO

A TEXT BOOK OF
THERMO-CHEMISTRY
AND
THERMODYNAMICS

BY

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LATE OF THE KGL. FRIEDRICH-WILHELM UNIVERSITY IN BERLIN

TRANSLATED AND REVISED

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PREFACE TO THE GERMAN EDITION

EVERY one will admit that a thorough understanding of physical chemistry, and of the success of its application in science and in technology, can only be obtained on the basis of thermodynamics.

Every chemist and every physicist who desires to take part in the development of physical chemistry must therefore be master of the principles of thermodynamics, and of the application of these principles to special problems.

This text-book is meant for those who desire to acquire a knowledge of the essential facts, and at the same time is intended as a review of what has hitherto been attained in the subject.

In the selection and arrangement of the material, I have been guided mainly by didactic considerations, and have purposely refrained from attempting an exhaustive account of the subject. I have endeavoured to present the contemporary state of thermodynamics as it may be deduced most simply from certain general empirical laws, and not as it has been developed historically.

I assume that the reader is master of the fundamental principles of physics and chemistry, and has some knowledge of the differential and integral calculus, but the most important chapters of the book will probably be intelligible even to those who are deficient in the latter particular.

I have illustrated every important formula by means of numerical examples, in order to facilitate the comprehension and

the application of the thermodynamical equations. On the other hand, I have restricted the description of the experimental methods as much as possible, in order not to exceed the dimensions suitable for a text-book. As a rule, I have merely sketched the principle of the method and have given references to detailed descriptions which are to be found in the many excellent books of reference.

I have made use of the kinetic theory of matter to supplement the thermodynamical demonstrations, in so far as this seemed suitable to me for the purpose of this text-book.

I have treated, very briefly, therefore, the newest development of the kinetic theory, viz., the theory of the elementary quantum of action, which in our present state of knowledge cannot yet be considered as conclusively established.

The data given in the tables were taken for the most part from the third edition of Landolt and Börnstein's tables, and from the second edition of Winkelmann's *Handbuch*.

In certain cases use was made of the proof sheets of the fourth edition of Landolt and Börnstein, which is to appear in autumn of this year. I am much indebted to the courtesy of the publishers of the tables, Julius Springer, who, with the permission of the editors, Geheimrat Börnstein and Professor W. A. Roth, were kind enough to place the proofs at my disposal.

I wish to express my hearty thanks to these gentlemen for their support in this matter.

O. SACKUR.

BRESLAU,
12*th April*, 1912.

TRANSLATOR'S PREFACE

When I undertook the translation of this book I was requested by the late Professor Sackur to make any alterations which seemed to me to be necessary, and to state in the preface where such alterations had been made. Many improvements were suggested by the author himself, and others were the result of correspondence between us. The alterations and additions for which I am alone responsible are as follows:

1. The discussion of the theory of Debye, p. 37.
2. The first part of the section on irreversible processes, p. 143, line 25, to p. 146, line 27.
3. The chapter on thermodynamic equilibrium in general (Chap. VI.), which takes the place of the section on "Freie Energie und thermodynamisches Potential" in the German edition.
4. Alterations in the discussion of the principle of Le Chatelier, Chap. VII. sect. 2.
5. Alterations in the discussion of the displacement law of Wien, Chap. XIII. sect. 4.
6. The section on the distribution of energy in the spectrum (Chap. XIII. sect. 5), which has been completely rewritten.

G. E. GIBSON.

Chemical Laboratory
of the University of California,
Berkeley, *June* 21*st*, 1916.

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CHAPTER I.

INTRODUCTION.

1. The conceptions of temperature, of heat, and of specific heat.

We owe our knowledge of temperature to the direct action of the senses. By touching a body we can tell whether it is hot or cold, and it is neither possible nor necessary to define the conceptions "hot" and "cold," nor to trace their origin back to other conceptions. We attribute our sensation of temperature to what we may call the thermal condition of the body; if a body appears to be hot or warm, we say that there is much heat in it; if cold, that it contains little heat, much, for example, as we say that a body appears bright when it is emitting much light, and dark when it is emitting little or none.

When two similar bodies are equally hot or cold to the touch, they have the same temperature, which remains unaltered if we bring the bodies into contact. On the other hand, a gradual change in temperature takes place if we bring into contact two or more similar bodies which do not feel equally hot or cold, *i.e.* have not the same temperature. The bodies which were hotter at the beginning cool down, while the colder bodies become warmer, until, ultimately, all have attained the same temperature. We conclude from this that the colder bodies take up heat, and that the warmer bodies give out heat, or that heat flows from places of high temperature to places of low temperature. For this reason, heat was considered to be fluid in nature for many years. It was looked upon as a substance with the properties of an imponderable fluid, which permeated

all bodies and determined their temperature, according to the amount of it which they contained.

If we wish to study the laws of the flow of heat, we must introduce exact measures for the merely psychological conceptions of heat and temperature, which we have been considering hitherto. Our sensation of temperature cannot help us in this, as sensations cannot be compared with one another quantitatively. We cannot perform a measurement of heat or of temperature until we have found some physical property of a body which varies uniquely and continuously with its thermal condition, and which can be measured in time and space by one of the ordinary scientific methods. Fortunately experiment has shown us that there are a great many physical properties of bodies which vary uniquely in this way with their thermal condition, and which may all, therefore, be used for the measurement of heat or of temperature. Nearly all the physical properties of a body are altered when it is heated. One of the easiest properties to measure is the volume. A body occupies more space when it is hot than when it is cold. We say, therefore, that heat causes expansion, and cold causes contraction. The property of expansion on heating is common to all bodies with very few exceptions (one exception is water between 0° and 4° C.), and is generally used as the basis of temperature measurements.

The expansion on heating is most marked in the case of gases, and was noticed first in them; as early as 100 B.C., we find this property of gases made use of by Hero of Alexandria in some ingenious experiments. In the case of liquids and solids the expansion is much less noticeable; in the latter case it is even somewhat difficult to determine. Gases and liquids are most suitable for the measurement of temperature, and for the construction of temperature measuring instruments, or thermometers, as they are called.

The gas thermometer was discovered by Galileo.* Liquid thermometers were introduced later. Fig. 1 is a diagram of Galileo's air thermometer, Fig. 2 of a liquid thermometer as used at the present day.

The temperatures which a body may assume constitute a

* Mach, *Prinzipien der Warmelehre*, 2nd ed. p. 6.

continuous series, which we may represent by the points of a straight line. Two fixed points are therefore necessary for the definition of a scale or measure of temperature. The distance between these points is divided into a number of equal parts or degrees. We can then record any given temperature as the distance from one of the fixed points, just as we record the position of a point on a line. Celsius chose the boiling point and the freezing point of water at the pressure of the atmosphere as the arbitrary fixed points of his scale of temperature, and divided the distance between them into 100 equal parts. The freezing point of water is taken as 0°; colder temperatures are reckoned negative, and warmer temperatures positive. The boiling point is thus 100° C. Réaumur divided the interval between the same fixed points into 80 parts; Fahrenheit chose as his zero point, the temperature which is produced by mixing ice, water, and solid ammonium chloride (−18° C.), and divided the interval between this temperature and the freezing point of water into 32 parts. The Celsius or centigrade scale of temperature is used for scientific purposes in all civilised countries nowadays.



Fig. 1.

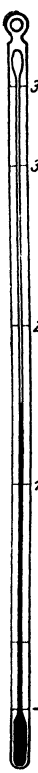


Fig. 2.

Liquid thermometers (Celsius), as shown in Fig. 2, are generally filled with mercury, and are standardised by immersing them first in freezing, and then in boiling water. When we have marked a scale of divisions on the thermometer, we can tell its own temperature without further trouble by noting the height of the liquid in the capillary. We are not, however, justified in using a thermometer of this sort to measure the temperature of other bodies, until we have considered the following experimental facts:

As stated above, a definite final temperature is reached when two bodies which are not equally hot are brought into contact. The greater the difference in size between the two bodies, the nearer is the final temperature to that of the larger body.

Contact with the thermometer will, strictly speaking, always alter the temperature of the body whose temperature we wish to determine, but this alteration will be negligible if the mass of the thermometer is very small in comparison with the mass of the body. In this case the thermometer will register correctly the previously unknown temperature of the body.

Experiment shows, further, that two bodies, which have the same temperature, are in temperature equilibrium with a third body, when the temperature of the third is equal to the temperature of the first two. From this it follows, that bodies which are equally hot show the same temperature on the thermometer.

After the discovery of the thermometer it became possible to study the interchange of heat between hot and cold bodies. The results of this investigation are as follows: When 1 kg. of water at 100° C. is mixed with an equal quantity of water at 0° C., the resulting mixture assumes a temperature of 50° C. If 2 kg. of water at 100° C. are mixed with 1 kg. at 0°, we obtain a temperature of $66\frac{2}{3}$° C., if 9 kg. at 100° are mixed with 1 kg. at zero, we obtain water at 90°, and so on. It appeared plausible therefore to regard the heat "substance," like other material substances, as indestructible, and, therefore, to apply to it a law of conservation. From this it followed that the total heat content of a system would be unchanged by the equalisation of the temperature of its parts, and therefore that the heat which is absorbed by the cold bodies in the process of heating up is exactly equal to the heat which is set free by the cooling of the hot bodies.

The heat Q, therefore, which will heat a body of mass m from the temperature t_1 to the temperature t_2, is proportional to its mass m and to the difference in temperature $t_2 - t_1$; and the above experiments are all in agreement with the equation:

$$Q = cm_1(t_2 - t_1) = cm_2(t_3 - t_2),$$

where t_1 and t_3 are the initial temperatures, t_2 is the final or equilibrium temperature, and c is a constant which for the meantime we shall leave indefinite. The final temperature is therefore:

$$t_2 = \frac{m_1 t_1 + m_2 t_3}{m_1 + m_2}.$$

We get the same results if we mix portions of other substances with each other, instead of water, such as mercury with mercury, or oil with oil, or if we bring two portions of the same kind of solid into contact. The interchange of heat takes place much more slowly in the latter case, as two solids cannot be brought into such intimate contact with each other as is possible with liquids, and the process is, therefore, more difficult to follow experimentally.

If, however, we mix two different substances with each other, such, for example, as water with oil or with mercury, we find that the result of the equalisation of temperature is quite different.

Thus, if we mix 1 kg. of water at 100° with 1 kg. of turpentine at 0°, the resulting temperature is 71° ; if we mix 1 kg. of water at 100° with 1 kg. of mercury at 0°, the equilibrium temperature is as high as 96·8°. The same amount of heat is required to heat the turpentine or mercury from 0° up to the equilibrium temperature as is gained by cooling the water from 100° to the equilibrium temperature, and hence a much smaller quantity of heat will suffice to raise a given weight of either of these two substances 1° than is necessary to raise the same weight of water 1°. The constant c of equation (1) has, therefore, a different value for each substance. c is called the specific heat of the substance. The specific heat of water is taken as unity, in analogy with the definition of specific gravity. This arbitrary definition enables us to introduce a measure for the amount of heat which a given body takes up or gives out. From the equation $Q = cm(t_2 - t_1)$, it follows that the unit of heat is the amount of heat which is necessary to raise unit mass of water (1 gram) 1° C. This unit of heat is called one calorie. The specific heat of a substance is, therefore, the number of calories which unit mass of the substance takes up when its temperature is raised 1°. Experiment has shown that the specific heat of almost all substances is less than unity. The amount of heat which is necessary to raise 1000 grams of water 1° C. is called a great calorie. It is usual to use the contractions " cal." for the small calorie, and " Cal." for the great calorie, so that we have 1 Cal. = 1000 cal.

We can now make use of the data given above to calculate the specific heat of mercury and of turpentine.

From the equation

$$Q = c_1 m_1 (t_2 - t_1) = c_2 m_2 (t_3 - t_2),$$

since $c_2 = 1$, $m_1 = m_2 = 1$, $t_1 = 0°$, $t_3 = 100°$, $t_2 = 71$, it follows that for turpentine

$$c_1 = \frac{c_2 m_2 (t_3 - t_2)}{m_1 (t_2 - t_1)} = \frac{29}{71} = 0{\cdot}41,$$

and for mercury, since $t_2 = 96{\cdot}8$, $c_1 = \frac{3{\cdot}2}{96{\cdot}8} = 0{\cdot}033$.

The experiments described in this paragraph are the basis of thermometry and of calorimetry, that is, of the scientific measurement of temperatures and of quantities of heat. The advance of science has brought with it considerable alterations and improvements in the methods of measurement. Some of the more important methods in use at the present day will be described in the following pages.

2. Thermometry.

The instruments used in the measurement of temperature may be divided into five classes, namely :

1. Liquid thermometers.
2. Gas thermometers.
3. Resistance thermometers.
4. Thermocouples.
5. Optical thermometers (for very high temperatures only).

(1) Liquid thermometers. A liquid suitable for use in a thermometer must fulfil the following conditions. It must remain liquid over a large range of temperature, and its boiling point and freezing point must be as different as possible from the mean temperature of our surroundings. It should not wet glass, which, on account of its transparency, is the only material suitable for the containing vessel. The liquid must also have a low specific heat, and must be capable of easy purification. Of all known substances, mercury is the only one which complies with all these conditions. On this account, alcohol, which was used formerly in the construction of thermometers, has been supplanted by mercury almost entirely. Toluol, which has been proposed recently as a thermometric fluid, shares with mercury the property, that its boiling point, unlike that of alcohol, does

not lie between 0° and 100° C. It is inferior, however, to mercury in other respects. Pentan or alcohol thermometers are used for temperatures at which mercury is solid (below −39°). For temperatures near or above the boiling point of mercury, the ebullition of the mercury is prevented by filling the empty part of the capillary with nitrogen, which is under considerable pressure at the higher temperatures. With this device it is possible to measure temperatures up to 500° with glass thermometers, and by using quartz instead of glass the range may be extended even as far as 750°.

A maximum thermometer is a thermometer which will register the highest temperature to which it has been subjected throughout a period of time during which the thermometer is not kept under continuous observation. For this purpose a small portion of the thread is kept separate from the main bulk of the mercury by a small bubble of air. As the temperature rises, the detached portion of the thread is pushed forward by the pressure of the air, and is held in position when the temperature falls by the friction of the glass walls. Another device which is used for this purpose depends on the fact, that a thread of mercury breaks very easily at a constriction. By constricting the capillary close to the bulb of the thermometer, we can cause the thread to break when the temperature falls, and thus indicate the highest temperature attained. In both forms the continuity between the detached thread and the main mass of the mercury can be re-established by shaking.

Maximum thermometers of this sort have found considerable application in meteorology, and for the measurement of the blood temperature in medicine.

(2) **Gas thermometers.** The use of gases for thermometers is simplified by the fact, that the expansion of all gases obeys very nearly the same law as the expansion of mercury. When their temperature is raised one degree, all gases expand by a constant amount which is independent of the temperature and of the nature of the gas. (Cf. Chap. II.) In the case of mercury, this uniformity of expansion is a necessary consequence of the definition of the Celsius scale of temperature, since the total expansion between 0° and 100° was divided into 100 equal parts.

Had we chosen another liquid instead of mercury for the definition of our scale of temperature, the correspondence between the degrees of the gas and liquid thermometers would probably have been much less exact. Even in the case of the mercury thermometer, there is no absolute correspondence, but the discrepancy between the various gas thermometers and the mercury thermometer is so small at ordinary temperatures, that it may be neglected for most practical purposes. The scientific standard of temperature is not the mercury, but the hydrogen thermometer. The deviation of the mercury thermometer from the air or the hydrogen thermometer is only a few hundredths of a degree at temperatures between 0° and 200°. At 300°, however, the difference is nearly 2°.*

The volume of a given quantity of gas depends on the pressure as well as on the temperature, and the pressure of a quantity of gas which is kept at constant volume depends on the temperature. We must, therefore, distinguish between two forms of gas thermometer, the constant pressure thermometer and the constant volume thermometer.

Fig. 3 is a diagram of a constant pressure thermometer, described by Regnault. A is the bulb of the thermometer, in which the gas is contained. The tubes cd and ef both contain mercury, and are in communication with each other at their lower extremities. The tube cd is calibrated. When A is heated or cooled, the level of the mercury is altered in both tubes. By adding some mercury at f or by letting some out at r, we can bring the mercury to the same level in both tubes. The pressure inside A is then equal to the pressure of the atmosphere. As this pressure is not absolutely constant, the temperature readings will only be accurate so long as the barometric pressure is unchanged.

The constant volume gas thermometer. We shall show in Chap. II. that the pressure of a gas at constant volume is altered by a constant amount when its temperature is raised by 1° C. We can, therefore, determine the temperature by means of this increase in pressure. Fig. 4 is a diagram of a thermometer of this sort. The bulb A of the thermometer contains a quantity of gas which is shut off from the outside air by means of a column

*Cf. Winkelmann, *Handb. d. Physik*, 2nd ed. p. 141.

of mercury in S, which in turn communicates through a flexible rubber connection with mercury in the tube n. By vertical displacement of n it is possible at any temperature to bring the meniscus back exactly to the same place S, which is distinguished by a mark, generally the extremity of a fine glass point, which is made to coincide exactly with the surface of the meniscus.

The difference in pressure which is necessary to effect this is given by the difference in level between S and n.*

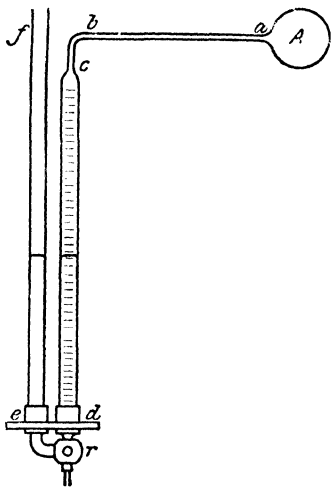


FIG. 3.

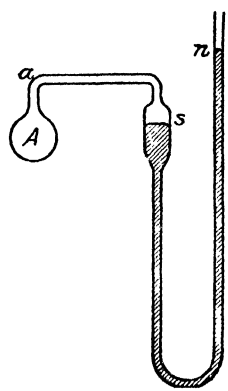


FIG. 4.

The lower limit to the utility of the gas thermometer is determined by the condensation of the gas. The hydrogen thermometer, however, and better still the helium thermometer, may be used down to exceedingly low temperatures. Theoretically, there is no upper limit to the applicability of the gas thermometer, but in practice the difficulty of finding a material of which to make the containing vessel, which will not become permeable to gases at high temperatures, makes it scarcely possible to measure temperatures above 1600° † in this way.

* A new form of gas thermometer is described by Miller, *Phil. Mag.* (6) **20**, 296. See also Travers and Jaquerod, *Zeit. Phys. Chem.* **45**, and Chappuis, *Mém. et Trav. du Bureau Intern. des Poids et des Mesures*, 1907.

† Holborn and Wien used an air thermometer for temperatures up to 1400° C. The containing vessel was made of porcelain, glazed on the outside. Even this material is permeable at high temperatures, but can be used when

Electrical methods. The electrical methods of measuring temperature are based on two facts, firstly, that the resistance of a conductor varies with the temperature, and secondly, that the electromotive force which is produced at a point of contact between two different metals or alloys is likewise a function of the temperature. If, therefore, we close a circuit consisting of two wires of different metals, so that there are two joints in the circuit where two metals meet, a current will flow in general so long as these joints are not at the same temperature. If the temperature of the one joint is known, a measurement of the electromotive force enables us to determine the temperature of the other. On account of the great sensibility of electrical measurements, it is possible to measure very small differences of temperature by either of these methods. They have the further advantage over the first and second methods, that we are enabled by their means to measure very high and very low temperatures in a most convenient manner. The small bulk occupied by a thermocouple is often important from an experimental point of view, and for this reason thermocouples are preferable in some cases to all other forms of thermometer.

Resistance thermometers. The resistance of all metals increases with the temperature. This variation may be represented with a good degree of approximation by the empirical formula

$$t_1 - t = A(w_{t_1} - w_t) + B(w^2_{t_1} - w^2_t),$$

where w_t is the resistance and t is the temperature.

The constants A and B may be calculated from the experimentally determined values of the resistance at two or more known temperatures. The formula may then be used to calculate the temperature from an experimental determination of the resistance. For the measurement of very small differences of temperature, such as are met with in the investigation of heat radiation, a very sensitive form of resistance thermometer is used, ordinarily known as the bolometer. This instrument

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the pressure inside the vessel does not exceed the external pressure. (*Wied. Ann.* **47**, 107 (1892).) Day and Sosman succeeded in measuring temperatures up to 1600° C. by means of a nitrogen thermometer with a bulb made of an alloy of platinum and rhodium. (*Amer. Jour. of Science*, (4) 29, 93 (1910).)

was first described by Langley.* It consists of a very thin strip of platinum foil, the resistance of which is determined with the aid of a very sensitive galvanometer. Differences of temperature of 10^{-6}° C. have been detected in this way. Less sensitive, but more generally useful resistance thermometers have been described by Jaeger and v. Steinwehr† and also by E. Haagn.‡ A thin platinum wire is wound while hot on a capillary tube of fused quartz about 2 mm. in diameter, which is then inserted into a slightly wider quartz tube, so that the spiral of platinum wire comes to lie in the annular space between the two tubes. The outer tube is then heated by means of the oxy-hydrogen flame until the quartz softens and collapses on the inner tube. In this way the platinum wire is completely imbedded in quartz, and follows any variation in the surrounding temperature practically instantaneously.

This instrument may be used for temperatures between $-100°$ and $+900°$ C.

At low temperatures the resistance of platinum is very small so that it is necessary to use very thin wires. §

Thermocouples. It is possible to arrange all metals and alloys in a series, such that every member of the series will become positively charged relatively to the next following member of the series, at the hot joint, in a circuit composed of these two metals. Pairs of metals, therefore, which are far apart in the thermoelectric series, will be most suitable for the measurement of temperature. Figs. 5*a* and 5*b* show two methods of using thermocouples for the measurement of temperature. *I* and *II* are the hot and cold joints, Me_1 and Me_2 are wires of the metals constituting the couple, and *G* is the galvanometer. A current will flow through the galvanometer as long as *I* and *II* are not at the same temperature. It may be necessary to allow for the fall in potential due to the resistance of the leads, or wires of the thermocouple. For very accurate measurements it is best to use a compensation method.

* Lummer and Kurlbaum, *Wied. Ann.* **46**, 204 (1892).

† *Ber. dtsch. physikal. Ges. 1903*, 353.

‡ *Zeitschr. f. angew. Chemie*, **20**, 565 (1907).

§ Cf. Kammerlingh Onnes, *Akad. von Wetensch.* Amsterdam, **19**, 1187 (1911).

We have the following relations between the temperature and the electromotive force E of a thermocouple. The total E.M.F. is the difference between the E.M.F.'s e_1 and e_2 at the hot and cold joints respectively. For a first approximation we may put

$$e = e_0 + at, \quad \ldots\ldots(1)$$

and hence $E = e_1 - e_2 = a(t_1 - t_2)$;

so that the E.M.F. of the couple is proportional to the difference in temperature between I and II.

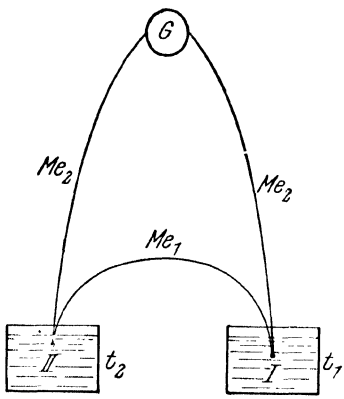


FIG. 5a.

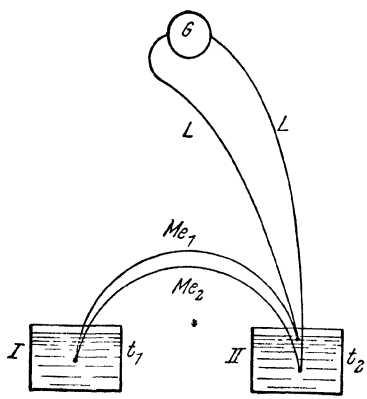


FIG. 5b.

The linear relationship only holds for very small differences of temperature, so that it is necessary in practice to go to a second approximation, viz.: $e = e_0 + at + bt^2$. .....(2)

We have then

$$\left.\begin{aligned} E = e_1 - e_2 &= a(t_1 - t_2) + b(t_1^2 - t_2^2) \\ &= a(t_1 - t_2)\left\{1 + \frac{b}{a}(t_1 + t_2)\right\}. \end{aligned}\right\} \quad \ldots\ldots(3)$$

This equation was given by Avenarius, and has been confirmed for a large number of metals over a considerable range of temperature. (See Chap. X.)

It is usual to choose the freezing point of water as the temperature of II, so that $t_2 = 0$. In this case the equation (3) for the E.M.F. of the thermocouple reduces to $E = at\left(1 + \frac{bt}{a}\right)$. Above

0° C. E will not rise steadily with the temperature unless $\frac{b}{a}$ is positive. If $\frac{b}{a}$ is negative, the curve of E against t will have a maximum, and every value of E will correspond to two distinct temperatures. For this reason pairs of metals for which $\frac{b}{a}$ is negative are unsuitable for use as thermometers at high temperatures. The couple silver-iron is an example of this.

For moderate and for low temperatures iron-constantan (an alloy of 60 per cent. copper with 40 per cent. nickel) is generally used.

This couple gives an E.M.F. of about $\frac{1}{20}$ millivolt per 1° C. For high temperatures, above the melting point of constantan, Le Chatelier's pyrometer is used. It is a thermocouple consisting of pure platinum and an alloy of platinum containing 10 per cent. of rhodium.

Holborn and Wien give the following equation for this couple :

$$t = 0{\cdot}1376E - 4{\cdot}841 \times 10^{-6}E^2 + 1{\cdot}378 \times 10^{-10}E^3,$$

where E is the E.M.F. in microvolts (10^{-6} volt).

Barus suggests an alloy of platinum with 20 per cent. of iridium, instead of rhodium, as the E.M.F. of this couple is about 23 per cent. higher than that of Le Chatelier's.

Silver-nickel is recommended as a thermocouple for moderate temperatures by Hevesy.* The sensibility is about 0·02 millivolt per 1° C. For very low temperatures Clay proposes the couple silver-gold.†

Thermometers, or thermocouples, whatever their nature, must be standardised over the whole range of temperature for which they are to be used. This may be done by comparison with an instrument which has already been standardised, or by the actual determination of temperatures which are accurately known and easily reproducible. For this purpose the thermometer is immersed in a bath in which some process is going on, which takes place at a constant and known temperature, such, for example, as the melting or boiling of a pure substance, or the

* *Physik. Zeitschr.* ii. 473 (1910).

† *Leiden Communications*, 107d (1908).

transition of one allotropic modification of a substance into another. (See Chap. II.)

The following are a few of the most easily reproducible processes of this sort. The temperatures at which they take place are very accurately known.

Boiling point of solid carbon dioxide (in presence of ether)	−78·3°*
Melting point of ice	0
Boiling point of water	100
Boiling point of naphthalene	218·0
Boiling point of sulphur	444·5
Melting point of antimony	630·7
Melting point of gold	1064

The optical methods for determining very high temperatures will be discussed in Chap. XII.

3. Calorimetry.

The determination of quantities of heat is important in a large number of physical and chemical problems. One of the most important of these is the determination of specific heats. The specific heat of a body is closely connected with its chemical nature, and is an exceedingly important quantity. Change of state (melting and evaporation with the reverse processes of solidification and condensation), all forms of chemical transformation, the creation and the disappearance of mechanical work, the conduction of electricity, the absorption of light and other forms of radiation, are all processes which involve transference of heat. The apparatus with which quantities of heat are determined are called calorimeters.

* See Ostwald-Luther, *Hand Hilfsbuch*, 3rd ed. p. 515. Day and Sosman give the following points between 300° and 1500° (relative to the nitrogen thermometer).

Melting point of	Zn	418·2
,, ,,	Sb	629·2
,, ,,	Ag	960·0
,, ,,	Au	1062·4
,, ,,	Cu	1082·6
,, ,,	Diopside	1391
,, ,,	Pd	1549
,, ,,	Pt	1755

(*Amer. Jour. of Science*, **29**, 93 (1910). See also Burgess, *Physik. Zeitschr.* **14**, 152 (1913), and Henning, *Zeit. El. Chem.* **19**, 185 (1913).)

(1) Calorimeters which depend on the law of mixtures. The basis of these calorimeters is the equation

$$Q = c_1 m_1 (t_2 - t_1).$$

If we desire to measure the quantity of heat Q, which is absorbed or liberated in any process, we arrange matters so that the process takes place in the interior of a known mass m, of a liquid of known specific heat c_1. t_1 is the initial, t_2 the final temperature of the calorimeter fluid. Q is therefore positive when the temperature of the liquid rises and heat is evolved by the system (*e.g.* combustion).

It is customary to consider quantities of heat given out from a body to its surroundings as positive, and quantities of heat absorbed from the surroundings as negative (*e.g.* latent heats of evaporation and of fusion). Whenever possible water is chosen as the calorimeter fluid, but at higher temperature it may be necessary to use liquids of higher boiling point, such as oil of turpentine or glycerine.

In making a determination it is necessary to consider a number of sources of error, and to correct for them. Thus we must make corrections for the change in temperature of the walls of the calorimeter vessel, of the thermometer itself, of the stirrer with which the liquid is agitated to secure efficient mixing, etc.

The reader must consult handbooks on laboratory practice for further details of the experimental methods, as space does not permit of their being described here.*

The determination of the specific heat of a body by means of the calorimeter which has just been described is carried out in the following manner. m_2 grams of the body under investigation are heated to the temperature t_3, and are then immersed in the calorimeter, which is initially at the temperature t_1. The temperature is then allowed to come to its final equilibrium value t_2. As the heat which is given out by the body is equal to the heat which the calorimeter absorbs from it, we have

$$Q = c_2 m_2 (t_3 - t_2) = c_1 m_1 (t_2 - t_1)$$

and

$$c_2 = \frac{c_1 m_1 (t_2 - t_1)}{m_2 (t_3 - t_2)}.$$

* Ostwald-Luther, 3rd edition; Kohlrausch, *Leitf. d. prakt. Physik*, etc.

At the same time, however, as the transfer of heat inside the calorimeter is going on, an interchange of heat with the surroundings is taking place.

It will not, therefore, be possible to obtain an absolutely constant final temperature in the calorimeter, unless this final temperature happens to coincide with the temperature of the surroundings. In general, therefore, there will always be a gradual change in the temperature of the calorimeter both before and after mixing has taken place. It is not possible, without further consideration, to calculate the temperature

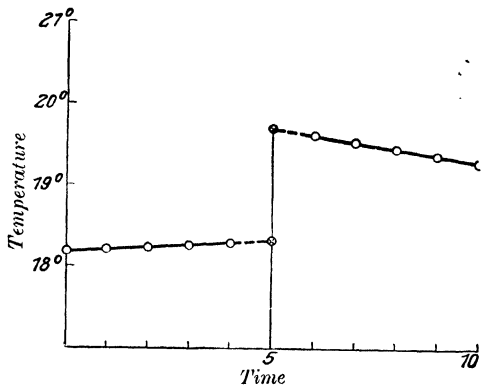


FIG. 6.

change $t_2 - t_1$, which would have taken place had all interchange of heat with the surroundings been excluded, and which alone is a measure of the quantity of heat given out by the body. In general, however, a fairly good approximation to this quantity can be arrived at in the following manner. The temperature in the calorimeter is observed at definite intervals of time before and after mixing, and the temperatures observed in this way are plotted on squared paper against the times. The curves obtained in this manner (see Fig. 6) are then extrapolated to an instant of time, at which we might imagine the mixing process to take place with infinite rapidity. The extrapolated values of the temperature at this instant of time are then read off, and are taken as the temperatures t_2 and t_1 in the above equation.

(2) The ice calorimeter. The form of ice calorimeter in use at the present day was invented by Bunsen, and is based on the observation that unit mass of every pure solid substance absorbs a perfectly definite amount w of (latent) heat in the process of melting.

If a solid body at its boiling point is allowed to absorb a quantity of heat Q, this quantity will cause m grams of the solid to melt, where m is determined by the equation $Q = mw$. If w is known we can arrive at Q by a determination of m.

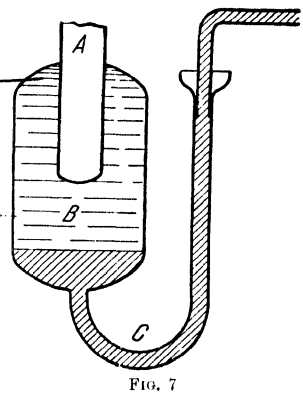


FIG. 7

The solid used in Bunsen's calorimeter is pure ice, which is kept at 0° C. by immersing the calorimeter (Fig. 7) in a mixture of crushed ice and water. The tube C is filled with mercury, while B contains water, part of which has been converted into ice by cooling the inside of the tube A with a freezing mixture. The heat evolution which we wish to investigate is then made to take place in A. As ice contracts on melting by an amount which has been measured very accurately, we can deduce the mass m of ice, which has been melted, from the displacement of the mercury meniscus on the calibrated extension of the tube C.

(3) The condensation calorimeter was recommended by Joly for the determination of specific heats. A perfectly definite quantity of heat l is necessary for the evaporation (as it is for the fusion) of unit mass of a substance. The amount of heat Q which is necessary to raise the temperature of a body from the initial temperature t to the boiling point t_2 of some liquid (*e.g.* 100° for water) is

$$Q = c_2 m_2 (t_2 - t).$$

To determine Q the body is suspended from the arm of a balance, and the air surrounding the body is then displaced by saturated vapour at a temperature t_2. Liquid condenses on the colder suspended body until its temperature has become equal to the temperature t_2 of the vapour. By determining the increase

in weight m, due to the adhering drops of condensed liquid, we can deduce Q from the equation,

$$Q = m_1 l = c_2 m_2 (t_2 - t_1) ;$$

and hence

$$c_2 = \frac{m_1 l}{m_2 (t_2 - t_1)}.$$

(4) **Electrical calorimeters.** It is possible with the aid of the electric current to produce heat and to measure its quantity with great accuracy. The experiments of Joule showed that a current of J amperes, flowing through a resistance of W ohms, produces in t seconds a quantity of heat $Q = kJ^2Wt$. The constant k is the number of calories which a current of 1 amp. produces per second in a resistance of 1 ohm, viz. $k = 0{\cdot}239$ cal. The determination of the specific heat of a liquid or a gas by this method is exceedingly simple. A conductor is immersed in the fluid, and a current of electricity is passed through it until a definite amount of heat has been produced. The rise in temperature of the fluid is then determined. If the body, which we wish to investigate, is a solid, *e.g.* a metal, a coil of wire is wrapped round it, and it is then immersed in some suitable fluid. The heating wire may be made to serve the purpose of a resistance thermometer as well. For some purposes, such as the measurement of the heat given out by a chemical reaction, or by the cooling of a body of unknown specific heat, it is advisable to determine the rise in temperature in the calorimeter produced by the process under investigation, and then to reproduce the same rise in temperature by electrical means. In this way the errors due to the interchange of heat with the surroundings, which are a disturbing factor in other methods, are very considerably reduced.

A number of other calorimeters which have been constructed for various special purposes will be described later on.

CHAPTER II.

THE BEHAVIOUR OF BODIES ON HEATING.

1. Conduction and radiation of heat; mean and true specific heat.

The heat content of a body can be increased in two ways. Heat may either be produced in the interior of the body itself (*e.g.* by chemical change or by the passage of an electric current) or it may be caused to pass into the body from a hotter body in its neighbourhood. In the latter case heat is carried by radiation or by conduction from the places of higher temperature to those of lower temperature; the hotter body acts as a source of heat. If the two bodies are only separated by a gas or by a liquid, the flow of heat may be aided by convection; that is to say, by currents which carry portions of the fluid, heated by contact with the hot body, into the neighbourhood of the colder body.

All substances in all states of aggregation have in a varying degree this power of conducting heat from places of higher temperature to places of lower temperature.

This fundamental property of matter must have its origin in the nature of heat itself. The fluid theory of heat assumed that the caloric fluid tended like a gas to distribute itself uniformly over the whole of the available space, and hence to travel from places of higher to places of lower density. The discovery that heat could be converted into mechanical work, and *vice versa*, led to the abandonment of the material theory of heat and to the acceptance of the kinetic theory, which looks upon heat as the kinetic energy of the ultimate particles of which

matter is built up. The more animated the molecular motion, the higher is the temperature of the body.

In the interior of the body, collisions between the ultimate particles must constantly be taking place. We suppose that in these collisions the particles communicate their kinetic energy to one another according to the ordinary laws of impact. For this reason, differences in temperature between bodies in contact cannot be permanent, so that we must ultimately arrive at a condition in which the mean kinetic energy and, therefore, the temperature of all the particles has become the same. This conception, which is the basis of the kinetic theory of gases, enables us to calculate the conductivity for heat in gases from their other physical properties. The nature of the molecular motion is not so well known for solids and for liquids as it is for gases, so that it is not yet possible to make an accurate picture of the mechanism of the conduction of heat through matter in these states of aggregation. The mathematical theory of the conduction of heat, which is independent of any special conception of the phenomena, was completely investigated by Fourier, and gives a formal representation of the observed facts for all bodies. Experiment has shown that all bodies which are good conductors of electricity, such as metals, are also good conductors of heat. The law of Wiedemann and Franz states that the ratio of the conductivity for electricity to the conductivity for heat is approximately constant for all bodies. In recent years this striking relationship has been explained by the modern theory of electrons, which supposes that the free negative electrons in metals move about freely like the molecules of a gas, and that the transfer of heat and of electricity is due to the motion of these electrons. The transfer of heat by conduction is a slow process, the velocity of which depends, in the first instance, on the conductivity. On the other hand, heat is radiated with an exceedingly great velocity in all directions of space and also through many media, such as the majority of gases, which are therefore said to be transparent to heat (diathermanous). Heat rays behave exactly like rays of light, and are governed by the same laws; they are absorbed and reflected by bodies in the same way as rays of light. A rise of temperature

in a body through which heat rays are passing takes place only when the rays are absorbed. During the conduction of heat the layers of matter surrounding the source of heat are heated one after the other, and at any instant there is a continuous fall in temperature from point to point of the conducting bodies until constancy of temperature has been reached. By radiation, on the other hand, an absorbing body at a distance from the source of heat may be heated while intermediate diathermanous layers remain cold. It is possible to ignite a body by concentrating the sun's rays on it by means of a convex lens of ice. In general, the transparency of various bodies is the same for heat as for light, but there are exceptions; water, for example, is opaque to heat rays, but is practically transparent to light. The laws of the radiation of heat will be discussed in greater detail in Chapter XII.

Let us now consider the changes which take place when a body has taken up heat in one or other of the above-mentioned ways. The first thing that we notice is that the temperature rises, and this rise in temperature is, as we know, $\frac{1}{mc}$ °C. for one calorie, where c is the specific heat, and m the mass of the body. This follows from the equation,

$$Q = mc(t_2 - t_1),$$

$$\text{or} \quad (t_2 - t_1) = \frac{Q}{mc}.$$

Experiment has shown that, for one and the same body, the rise in temperature, due to a given amount of heat, is not constant at all temperatures. In general it is smaller, the higher the temperature at which the heat is absorbed. For example, the temperature of 1 gr. of water at 15° C. is raised exactly 1°, *i.e.* to 16·000°, by the absorption of 1 calorie, while the same weight of water at 99° is only raised 0·992°, *i.e.* to 99·992°, by 1 cal. From this it follows that the specific heat c is dependent on the temperature, although only very slightly so. In the above example c must rise with increasing temperature, since the rise in temperature produced by a given amount of heat diminishes.

These facts make it necessary to define the conception "Specific Heat" more closely, and we are led to consider two new conceptions, viz. "True Specific Heat" and "Mean Specific Heat."

Considering unit mass of the substances, the above equation tells us that the specific heat c is given by the ratio of the quantity of heat Q necessary to produce the rise in temperature $t_2 - t_1$ to this same difference in temperature $t_2 - t_1$. In future this quantity will be called the "Mean Specific Heat" between the temperature t_1 and t_2, and will be written c_m. If we find that c_m has different values for different intervals of temperature $t_2 - t_1$, we must look upon c_m as the mean value of all the values which the specific heat has assumed in the interval of temperature $t_2 - t_1$. For a temperature t the specific heat must, therefore, have a definite numerical value, which we shall call the true specific heat c_w.

In order to determine directly the true specific heat at the temperature t, it would be necessary to make a determination of the mean specific heat for a very narrow range of temperature in which t were included. The smaller we take this range of temperature, the more nearly would the measurement of the mean specific heat give us the value of the true specific heat c_w. Identity of the two could only be attained by taking the interval $t_2 - t_1$ infinitely small. For $t_2 - t_1$ we may then write the differential dt. In this limiting case we have $c_w = \frac{dQ}{dt}$, or in words: the true specific heat at the temperature t is the ratio of the infinitely small quantity of heat dQ to the infinitely small rise in temperature dt which it produces in unit mass of the body. From these considerations it is clear that c_w can never be measured directly. We can, however, deduce its value, if we know the way in which the mean specific heat varies with the temperature.

The relationship between c_m and c_w can be stated mathematically as follows:

Let Q be the quantity of heat which is necessary to raise the temperature of unit mass of a body from t_1 to t_2; then the mean specific heat between t_1 and t_2° is

$$c_m = \frac{Q}{t_2 - t_1}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The true specific heat for any temperature t between 0 and t_1 is

$$c_w = \frac{dQ}{dt}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

and hence, by integrating (2), the quantity of heat Q which is necessary to raise the temperature from t_1 to t_2 is

$$Q = \int_{t_1}^{t_2} c_w \, dt,$$

and by combining this with (1), we get

$$c_m = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} c_w \, dt. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Equation (3) enables us to calculate c_m if we know c_w as a function of the temperature. Generally, however, we wish to calculate c_w, having determined c_m by experiment as a function of $t_2 - t_1$.

From (1) and (2), we have

$$c_m(t_2 - t_1) = Q = \int_{t_1}^{t_2} c_w \, dt. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

By differentiating (4) with respect to t_2, we get

$$c_w = \frac{dc_m(t_2 - t_1)}{dt_2} = (t_2 - t_1)\frac{dc_m}{dt_2} + c_m. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Thus, for example, if we had found the mean specific heat between 0 and $t°$ to be a linear function of t, say

$$c_m = a + \beta t,$$

we should have, by (5), $\quad c_w = a + 2\beta t,$

i.e. also a linear function. If

$$c_m = a + \beta t + \gamma t^2,$$

we find $\quad c_w = a + 2\beta t + 3\gamma t^2,$

and so on.

The fact that the specific heat of a body is a function of its temperature leads us to a closer definition of the unit of heat, the calorie.

In Chapter I. we defined this unit as the amount of heat which is necessary to raise the temperature of 1 gram of water 1° C. If the specific heat of water at 0°, however, is not the

same as at 100°, the amount of heat which is necessary to raise a gram of water from 0° to 1° will not be the same as the amount that is required to raise it from 99° to 100°.

It is customary to choose as unit, either the amount of heat which will raise 1 gram of water from 14·5° to 15·5° C (15° calorie), or the hundredth part of the amount of heat which will raise 1 gram of water from 0° to 100° C. (mean calorie).

The mean of several accurate determinations of the relationship between these two units gives for the ratio

$$\frac{\text{mean calorie}}{15^\circ \text{ calorie}} = 1{\cdot}0002.*$$

For most purposes the two units may be regarded as identical.

2. The specific heat of solids.

(*a*) *At moderate and high temperatures.* The specific heat of all solids rises with the temperature, although at very different rates for different substances. In many cases it is possible to represent this variation by means of a linear equation, as $c_w = a + \beta t$; in other cases it is necessary to add a quadratic term, so that $c_w = a + \beta t + \gamma t^2$. As γ is always found to be very small, the linear equation suffices for small ranges of temperature in all cases.

The following table gives the values of β and γ which have been found for a number of solids. The highest temperature for which the equation is applicable is given in the last column.†

Substance.	a	β	γ	t
Silver ‡	0·0545	0·00002141	—	300°
Copper ‡	0·0920	0·00002125	—	300°
Nickel ‡	0·1043	0·00009460	—	300°
Iron (pure) §	0·11012	0·0000506	0·000000164	660°
Fused quartz §	0·1737	0·000394	0·000000027	600°

* Callendar and Barnes, see Ostwald-Luther, 3rd edition, p. 303.

† For recent measurements of specific heat at high temperatures see Magnus, *Phys. Zeit.* **14**, 5 (1913).

‡ Naccari, quoted from Winkelmann, vol. iii. p. 180.

§ Pionchon, quoted from Winkelmann, vol. iii. p. 181.

Calculating from this table, we find the true specific heat of silver at 100° to be 0·0566. The mean specific heat between 0 and t is, according to p. 23, $c_m = a + \frac{\beta t}{2} + \frac{\gamma t^2}{3}$. Hence, for silver between 0° and 100° C., $c_m = 0{\cdot}0555$.

The specific heat varies most rapidly with the temperature in the case of non-metals of low atomic weight. Particularly is this true of carbon, above all in the non-conducting crystalline form of diamond. The specific heat of diamond increases from 0·1128 to 0·46, that is to say, about four-fold in the interval between 0° and 1000°.

(*b*) *At low temperatures.* The specific heat decreases still further at temperatures below zero. Behn* gives the following figures for the mean specific heat of the metals:

Substance.	(i) +100° to +18°	(ii) +18° to −79°	(iii) −79° to −186°	$c_{(i)} : c_{(iii)}$
Lead - - -	0·0310	0·0300	0·0291	1·06
Platinum - -	0·0324	0·0311	0·0277	1·17
Copper - - -	0·094	0·0883	0·0716	1·31
Nickel - - -	0·10	0·0983	0·0743	1·47
Iron - - -	0·113	0·0959	0·0721	1·57
Aluminium - -	0·22	0·195	0·153	1·43

The smaller the atomic weight of the metal, the more rapidly the specific heat decreases with the temperature. The variation of the specific heat at very low temperatures will be discussed later on.

Specific heat and chemical character. In 1819 Dulong and Petit discovered the following law: The product of the atomic weight and the specific heat is a constant, namely 6·4, for all elements in the solid state. The atoms of the elements have all, therefore, the same specific heat (atomic heat). The following table shows that this law only holds approximately, and that several of the elements are exceptions to it, if we take the specific heat at the ordinary temperature as the basis of our calculations. The values of c are taken from the third edition of Landolt and Börnstein. The values of the true specific heat at room temperature were taken wherever possible. When

* *Wied. Ann.* **66**, 235 (1898).

the true specific heat could not be obtained, the mean specific heat at the ordinary temperature is given in the table:

Element.	A	c	$A.c$
Aluminium	27·1	0·222	6·0
Antimony	120	0·0489	5·9
Arsenic (crystalline)	75	0·083	6·2
Lead	207	0·0299	6·2
Bromine (solid)	80	0·0843	6·7
Caesium	133	0·0482	6·4
Cadmium	112	0·055	6·2
Chromium	52	0·104	5·4
Iron	56	0·110	6·2
Calcium	40	0·180	5·4
Gold	155	0·031	6·1
Indium	197	0·060	6·9
Iodine	127	0·0541	6·9
Iridium	193	0·0323	6·2
Potassium	39	0·166	6·5
Cobalt	59	0·103	6·1
Copper	63·6	0·0925	5·9
Lithium	7·0	0·941	6·6
Magnesium	24·3	0·246	6·0
Manganese	55	0·122	6·7
Molybdenum	96	0·066	6·4
Sodium	23	0·293	6·7
Nickel	58·7	0·108	6·4
Osmium	191	0·0311	5·9
Palladium	107	0·059	6·3
Phosphorus (colourless)	31	0·20	6·2
Platinum	195	0·032	6·2
Mercury	200	0·032	6·4
Rhodium	103	0·058	6·0
Ruthenium	102	0·061	6·2
Sulphur (rhombic)	32	0·173	5·5
Selenium	79	0·084	6·6
Silver	108	0·055	5·9
Tellurium	127·5	0·048	6·1
Titanium	204	0·032	6·5
Uranium	48	0·112	5·4
Thallium	238·5	0·028	6·7
Bismuth	208	0·030	6·2
Tungsten	184	0·034	6·3
Zinc	65·4	0·0915	6·0
Tin	119	0·05	6·0

The elements of low atomic weight, such as boron, carbon, beryllium, and silicon, show the greatest deviations from this rule, and it is just for these elements, that we find the most rapid variation of the specific heat with the temperature. As we have shown, the temperature coefficient of the specific heat is different for each substance, so that the law of Dulong and Petit, even if it were true at one temperature, could not be true at all temperatures. At high temperatures the atomic heats of the lighter elements approximate to 6·4. H. F. Weber* gives the following figures :

Substance.	A	t	c	$A.c$
Boron - - -	11·0	26·6	0·2382	2·6
		233·0	0·3663	4·04
		Red heat	0·50	5·5
Diamond - -	12·0	10·7	0·113	1·25
		985·0	0·459	5·5
Silicon (cryst.) -	28·3	21·6	0·170	4·8
		232·4	0·203	5·75
Beryllium † - -	9·1	0°	0·376	3·4
		100	0·476	4·2
		300	0·591	5·3
		500	0·621	5·6

The law is not universally true, nevertheless, even at high temperatures, as the atomic heats of the heavy metals rise to much above 6·4, thus, for iron at 660 (see p. 24),

$$cA = -0{\cdot}20 \times 55{\cdot}9 = 11{\cdot}8.$$

The agreement between the atomic heats becomes somewhat better if we compare them at so-called comparable (*vergleichbaren*) temperatures, instead of at the same temperature. Lämmel ‡ chose the melting point, or some definite fraction of the melting point on the absolute scale, as a comparable temperature. The atomic heats of nearly all elements, at their melting

* *Pogg. Ann.* **154**, 575 (1875).

† Humpidge, *Proc. Roy. Soc.* **39**, 1 (1885).

‡ *Ann. d. Physik*, (4) **23**, 61 (1907).

points, lie between 9 and 10. If we take half the melting point as the comparable temperature, the atomic heats all lie between 6 and 7. We must not, however, attach too great importance to this relationship, as we cannot test it for carbon, which is the most important exception to Dulong and Petit's law, since the melting point of carbon is unknown.

There is another fact which shows us that the law of Dulong and Petit cannot be strictly true. Many elements are capable of existing in several modifications which are distinguished from one another by their crystalline form, by their specific gravity, and by many other physical properties. These allotropic modifications have not the same specific heat, so that the atomic heat is not even constant for one and the same element. Still less, then, can we expect it to be constant for all elements. Wigand * has shown that the denser modification of an element has always the smaller specific heat, as may be seen in the next table.

The remarkable relationship between density and specific heat is an important confirmation of a theory of Richarz, who deduces the limits of the applicability of Dulong and Petit's law, and the abnormal behaviour of the lighter elements from kinetic considerations.† According to Richarz, the law of Dulong and Petit can only be strictly true, when the displacements of the atoms from their positions of equilibrium, due to their heat motion, are small compared to the distance between neighbouring atoms. This will cease to be true (1) when the distance between the atoms is small, and (2) when the displacement of the atoms from their positions of equilibrium is great. The first case applies to substances whose density is great in proportion to their atomic weight, and whose atomic volumes are, therefore, small. The second case applies when the mass of the atoms is small, since for the same temperature and kinetic energy the smaller atoms must have the greater velocity.

* *Ann. d. Physik*, (4) **22**, 64 (1906).

† *Wied. Ann.* **48**, 708 (1893); *Zeit. f. anoryan. Chemie*, **58**, 356 (1908).

Substance.	Modification.	Density.	Specific Heat.	Temperature (for spec. heat)	Atomic Heat.
Carbon	diamond	3·518	0·1128	10·7	1·35
	graphite	2·25	0·1604	10·8	1·92
	retort carbon	1·885	0·2040	24–68	2·47
Boron	crystalline	2·535	0·2518	0–100	2·76
	amorphous	2·45	0·3066	0–100	3·37
Silicon	crystalline	2·49	0·165	21	4·7
	amorphous	2·35	0·214	21	6·05
Phosphorus	red	2·296	0·1829	0–51	5·66
	colourless	1·828	0·202	13–36	6·12
Sulphur	rhombic	2·06	0·1728	0–54	5·54
	monoclinic	1·96	0·1809	0–52	5·80
	amorphous insol.	1·89	0·1902	0–53	6·10
	amorphous sol.	1·86	0·2483	0–50	8·0
Arsenic	gray	5·87	0·0822	0–100	6·16
	black	4·78	0·0861	0–100	6·46
Selenium	crystalline	4·8	0·0840	22–62	6·65
	amorphous	4·3	0·1125	21–57	8·9
Tellurium	crystalline	6·3	0·0483	15–100	6·16
	amorphous	6·0	0·0525	15–100	6·70
Tin*	white	7·30	0·0538	0–19	6·40
	gray	5·85	0·0496	0–19	5·91

The deviations from Dulong and Petit's law will, therefore, be most noticeable for elements of small atomic weight A and small atomic volume V. This consequence of Richarz's theory is fairly well confirmed by the following table :

Element.	A	V	$A \cdot C$
Lithium	7	11·5	6·6
Beryllium	9·1	5·6	3·6–5·3
Boron	10·9	4·0	2·5–5·5
Carbon	12	3·6	1·4–5·5
Sodium	23	23·7	6·7
Magnesium	24	13·8	5·9–6·0
Aluminium	27	10·6	5·5–5·8
Silicon	28	11·2	4·6–5·7
Phosphorus	31	13·5	5·3–5·9
Sulphur	32	15·7	5·2–5·7
Potassium	39	45·4	6·5
Calcium	40	25·4	6·8

* Brönsted, *Zeit. el. Chem.* **18**, 714 (1912). Tin is an exception to Richarz's law.

Diminution of the atomic volume by mechanical compression lowers the specific heat.*

The reduction in the heat capacity of a system which is consequent on most spontaneous chemical reactions led Th. W. Richards to the hypothesis that the atomic volumes of the elements are diminished when they enter into combination. The action of the chemical forces may, therefore, be compared to a mechanical compression.†

All the values of the specific heat which we have been considering hitherto were obtained by allowing the bodies to absorb heat at atmospheric pressure, and permitting the expansion caused by the rise in temperature to take place. If, however, we carry out the determination under pressure in a closed vessel, so that the volume is kept constant, we find that a smaller amount of heat is necessary to raise the temperature of the body 1° than was necessary, when we permitted the body to expand against a constant pressure during heating. The specific heat of a body measured at constant volume is, therefore, smaller than the specific heat at constant pressure. For solid and liquid bodies the difference is very small, as the expansion on heating is insignificant. For gases, however, the difference is considerable. This will be considered later on, when we come to discuss the properties of gases.

The specific heat at constant volume c_v of solids and liquids cannot be measured directly. With the aid of thermodynamics, however, it is possible to deduce an equation connecting the specific heat at constant volume c_v with the coefficient of expansion, the compressibility and the specific heat at constant pressure c_p (see Chapter V.).

G. N. Lewis‡ has calculated the specific heat at constant volume in this way, and finds that all elements which have a higher atomic weight than potassium have an atomic heat approximately equal to 5·9. The deviations from this mean value are, on the average, 0·1 less than the corresponding deviations for c_p. Dulong and Petit's law, therefore, holds better for c_v than for c_p.

* Regnault, *Ann. Chim. Phys.* **73**, 5 (1890).

† *Zeit. f. phys. Chem.* **40**, 597. **42**, 129 (1903).

‡ *Zeitschr. f. d. anorgan. Chemie*, **55**, 200 (1907).

Although the law of constant atomic heats is only very approximately true, it has proved very useful in many branches of chemistry; for example, in the determination of atomic weights. Chemical analysis gives us only the equivalents. For example, the analysis of indium chloride shows that 38 parts of indium combine with 35·5 parts of chlorine, and hence the atomic weight of indium must either be 38·3, or an integral multiple of this number. By Dulong and Petit's law, we find the atomic weight to be $A = n \times 38{\cdot}3 = \frac{6{\cdot}4}{c}$, approximately. Since c is found to be equal to 0·061, this condition will be satisfied best if we put $n = 3$. Hence, the atomic weight of indium must be 115. From this it follows that indium must belong to the third group of the periodic system, which is in excellent agreement with the other properties of this element.

Specific heat of compounds. In 1831 F. E. Neumann stated the following law: The product of the specific heat and the molecular weight of substances which are similar in chemical character, is a constant. By similar in chemical character, Neumann means substances, such as metallic oxides of the formula MeO or MeO_2, metallic sulphides MeS, chlorides MeCl, and so on. The following table illustrates this law for metallic oxides of the formula MeO:

Substance.	M	c	$M \cdot c$
PbO	223	0·0512	11·4
CuO	79·4	0·013	10·3
MgO	40	0·244	9·8
MnO	71	0·157	11·1
NiO	74·8	0·159	11·9
HgO	216	0·053	11·7
ZnO	81·2	0·125	10·1
Mean	—	—	10·9

The agreement is, as we see, very rough, yet the values in the last column are always of the same order of magnitude. The agreement is much the same for other types of compounds. Neumann has calculated the mean values of a large number of

series of this sort. His results are given in the following table (under (i)):

		(i)	(ii) Number of atoms n.	(iii) $M \cdot c$ (calc.) $= n \times 6{\cdot}4$.	(iv)
Oxides	MeO	11·0	2	12·8	10·4
,,	MeO_2	14·0	3	19·2	14·4
,,	MeO_3	18·8	4	25·6	18·4
Sulphides	MeS	11·9	2	12·8	11·4
,,	MeS_2	18·1	3	19·2	16·8
Chlorides	MeCl	12·8	2	12·8	12·8
,,	$MeCl_2$	18·7	3	19·2	19·2
Iodides	MeI	13·4	2	12·8	12·8
,,	MeI_2	19·4	3	19·2	19·2
Nitrates	$MeNO_3$	24·0	5	32·0	24·8
,,	MeN_2O_6	38·2	9	57·6	42·8
Sulphates	$MeSO_4$	26·4	6	38·4	25·8
,,	Me_2SO_4	32·9	7	44·8	32·2
Carbonates	$MeCO_3$	21·4	5	32·0	20·2
,,	Me_2CO_3	29·1	6	38·4	26·6

The values in column (iii) were calculated on the simple assumptions that the atomic heats of all elements are equal to 6·4, and that this value is unaltered when the atoms undergo chemical combination, so that the molecular heat is simply the sum of the atomic heats. The table shows that this hypothesis is not in agreement with the facts. The differences between the calculated and observed values of the molecular heats (i) and (iii) are, for the most part, considerable. These deviations show that one or both of our hypotheses must be incorrect. Either the atomic heats of the elements are not all equal, or, in addition to this, there is an alteration in the specific heat when the atoms combine to form molecules. Joule and, after him, Kopp assumed that the first hypothesis only was at fault, and stated the law as follows: the molecular heat of a compound is the sum of the specific heats of the individual atoms composing the molecule. If the atoms A_1, A_2, A_3, etc., with the specific heats c_1, c_2, c_3, etc., unite to form the compound $A_1^{n_1}$, $A_2^{n_2}$, $A_3^{n_3}$ ... of molecular weight,

$$M = n_1A_1 + n_2A_2 + n_3A_3 + \ldots\ldots\ldots\ldots,$$

we obtain the equation

$$M \cdot c = n_1 c_1 A_1 + n_2 c_2 A_2 + n_3 c_3 A_3 \ldots\ldots\ldots\ldots$$

For all elements, except those of small atomic weight, we have $cA = 6{\cdot}4$ by the law of Dulong and Petit. The atomic heats of the lighter solids, and also of all gaseous elements at ordinary temperatures, must have a considerably smaller value than this, as the calculated values in column (iii) are much larger than the figures, found by experiment, in column (i). On the assumption that the law, which bears his name, was approximately correct, Kopp calculated the atomic heats of the elements, oxygen, hydrogen, fluorine, nitrogen, etc. The figures in column (iv) were calculated by him in this way. The values of the atomic heats of the elements which he used in the calculations are as follows :

O	H	F	B	C	Si	S	P
4·0	2·3	5·0	2·7	1·8	3·8	5·4	5·4

and all other elements 6·4.

Kopp's law, as we see, is only a very rough approximation to the facts. It does not hold as accurately as the law of Dulong and Petit. We need not be very much surprised at this, however, since what was said above about the limitations of Dulong and Petit's law is applicable to Kopp's law in a still higher degree. The specific heats of substances depend upon the temperature to a very varying extent. If the atomic heats are equal to one another, at one temperature, they must be different at other temperatures. In the same way the molecular heats must be unequal, in general, to the sum of the atomic heats, even if they happen to be the same at one temperature. According to the kinetic theory, the temperature coefficient of the specific heat depends upon the relative position and motion of the atoms. It is, at least, probable that both of these should be influenced in some unknown manner by the chemical forces between the atoms. For this reason, Nernst made the very plausible assumption that Kopp's law is accurately true when the heat motion of the atoms and molecules ceases, *i.e.* at the absolute zero. The confirmation of this assumption will be given in a later paragraph.

Einstein's* theory of specific heat leads to the same result. This theory connects the molecular motion in solid bodies with Planck's theory of radiation, and has been confirmed in the main by the experimental researches of Nernst and his collaborators in the last few years. Einstein assumes that the heat motion in solid bodies consists of vibrations of the atoms about a point of equilibrium, as distinct from the translational motion of the molecules which we assume for gases. The energy of these vibrations—and this is the characteristic feature of the theory, and also of Planck's theory of radiation—is always an integral multiple of a quantity of energy ϵ, which, in turn, is the product of a universal constant (*i.e.* a constant independent of the nature of the substance) and the frequency ν (number of vibrations per second), viz. $\epsilon = \frac{R}{N}\beta . \nu$. The frequency is independent of the temperature, and is a characteristic constant of the substance. Einstein obtained the following formula for the atomic heat at constant volume of an element containing vibrating particles of only one frequency :

$$A . c = C = 3R\left(\frac{\beta\nu}{T}\right)^2 \frac{e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2}.$$

For substances, the molecules of which contain vibrating particles of more than one kind—for example, compounds, and possibly also polyatomic molecules—we have the following equation :

$$C = 3R\sum\left(\frac{\beta\nu}{T}\right)^2 \frac{e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2},$$

where the summation refers to the values of ν corresponding to the various vibrating systems.

According to this new theory of specific heat, the specific heat of all solid bodies, and probably also of super-cooled liquids, vanishes at the absolute zero, and increases with the temperature in the manner shown in the curve (Fig. 8). For every substance there is a certain range of temperature in which the specific heat varies rapidly with the temperature. Above this

* *Ann. d. Physik.* **22**, 189 (1908).

temperature, the gradient becomes less, and the atomic heat approaches asymptotically the limiting value, for $T=\infty$, of $3R=6$.* The position of this critical range of temperature is determined for each substance by the numerical value of the frequency ν. The greater ν, the higher is the temperature at which this rapid increase of the specific heat takes place, and the longer does it take for the specific heat to reach its maximum value.

This theory gives an approximate representation of the facts which have been observed hitherto. All substances which obey Dulong and Petit's law at ordinary temperatures (for which $c_v=5{\cdot}9$ approximately) are beyond this region of rapid increase at room temperature. For the lighter elements, such as carbon, boron, and so on, the specific heat is still at a considerable distance from its maximum value. These elements, therefore, must have a much greater frequency than the heavier elements.

On the other hand, we should expect that elements, which obey Dulong and Petit's law at the ordinary temperature, would have much too small values of the specific heat at lower temperatures. When Einstein first propounded his theory, there was nothing to indicate a decrease of the specific heat to the value 0, although it was known that the specific heat of all substances diminished when the temperature was lowered. Of late, however, the researches of Nernst and his collaborators have shown that the specific heats of all substances, whether amorphous or crystalline, become very small if the temperature is lowered sufficiently. They made determinations down to the boiling point of hydrogen ($-253°$ C.), and found that their results could be represented by curves of the form shown in Fig. 8. In the case of diamond, they have succeeded in reaching the region before the rapid increase, in which the specific heat is practically

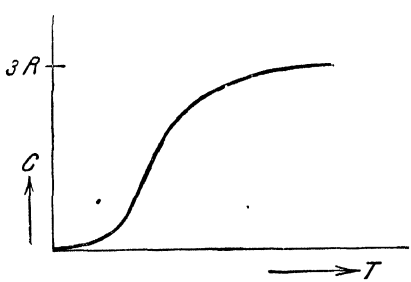


FIG. 8.

* The numerical value of R is 2 cal. per degree.

zero, so that even a very small absorption of heat is accompanied by a large rise in temperature.

The method of determining the specific heat which was used by Nernst and his collaborators was devised by Eucken.* The substance was immersed in a suitable bath, such as liquid hydrogen, or liquid air, in a vacuum vessel, and was then heated by a known electric current. The heating wire also served as a resistance thermometer. As the rise in temperature was always very small, the true specific heat was obtained directly. The following table shows the more or less rapid decrease of the specific heat with the temperature for a number of substances: †

Diamond.	
t	C (for gr. atom), *i.e.* mean Atomic heat.
−53	0·72
−64	0·66
−68	0·62
−181	0·03
−186·5	0·03
−234, −227	0·00

Rhombic Sulphur.	
−188	2·84
−204	2·29
−216	2·06
−243·1	1·14
−244·7	1·08
−245·5	1·04
−247·1	0·99
−250·4	0·96

Potassium Chloride.	
t	C (for gr. atom), *i.e.* mean Atomic heat.
17	6·02
−187	4·36
−196·4	4·11
−203	3·79
−212·8	3·36
−215·4	3·06
−221·2	2·80
−224·7	2·85
−239·3	1·25
−242·9	0·98
−246·1	0·76
−250·2	0·58

Copper.	
185	3·38
−186	3·33
−239·6	0·538
−245·3	0·324
−249·5	0·223

While Einstein's theory gives a qualitative representation of the facts, there can be no doubt that the agreement is very rough. In the first place, the specific heat of all substances probably increases above the limiting value $3R$ with rise in temperature, and in the second place Nernst has found that there are systematic deviations from Einstein's formula at low temperatures. In conjunction with Lindemann he has pro-

* *Phys. Zeit.* **10**, 586 (1909). † Nernst, *Ann. d. Phys.* **36**, 295 (1911).

posed a formula of the same form as Einstein's, and which, like Einstein's, contains only one constant for each element. It is as follows:

$$c_p = \frac{3R}{2}\sum\left(\frac{\beta\nu}{T}\right)^2 \frac{e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}}-1\right)^2} + \frac{3}{2}R\sum\left(\frac{\beta\nu}{2T}\right)^2 \frac{e^{\frac{\beta\nu}{2T}}}{\left(e^{\frac{\beta\nu}{2T}}-1\right)^2} + aT^{\frac{3}{2}}.*$$

This equation agrees much better with the experimental facts than Einstein's, but must be regarded as entirely empirical.

Einstein's fundamental assumption that the atoms all vibrate with the same constant frequency is certainly incorrect. Debye† makes the more probable assumption that the atoms may vibrate with a large number of different frequencies. The slower vibrations of the atoms are simply the ordinary sound vibrations in the body, and are determined by its elastic constants (compressibility and Poisson's ratio). The maximum number of different vibrations which a system of N particles (atoms) is capable of executing can be shown to be equal to the degrees of freedom of the system, viz. $3N$. The upper limit to the atomic frequency is therefore finite, and can be calculated from the elastic constants of the body. This limiting frequency ν_m plays a somewhat similar part in Debye's theory to the constant atomic frequency ν in Einstein's theory. Assuming that the energy of each of the possible atomic vibrations is an integral multiple of the quantum $\epsilon = \frac{R}{N}\beta\nu$, Debye obtains the formula:

$$\frac{c_v}{3R} = \frac{12}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3x}{e^x - 1},$$

where $x = \frac{\beta\nu_m}{T}$.

For very low temperatures this equation simplifies to

$$c_v = \text{const. } T^3 = 3R \cdot \frac{4\pi^4}{5}\left(\frac{T}{\beta\nu_m}\right)^3,$$

so that the specific heat at low temperatures is proportional to the cube of the absolute temperature. This law is in excellent

* The relatively small term $aT^{\frac{3}{2}}$ (a is a small quantity) corresponds to the work done by expansion against a constant pressure.

† *Ann. d. Phys.* (1912), p. 812.

agreement with experiment. At higher temperatures the values calculated from Debye's equation agree very closely with those calculated from the equation of Nernst and Lindemann.

If the atomic frequency ν has any real physical significance it should be possible to calculate it from various other physical properties. Thus Nernst supposed that the frequency of a body composed of electrically charged ions could be calculated from its optical properties. In agreement with this hypothesis he found that the frequencies of the ultra-red absorption bands of potassium and sodium chloride determined by Rubens were approximately equal to the values of ν calculated from the specific heat. It is probable, however, that this agreement is purely accidental.

Another method of calculating ν was obtained by Lindemann in the following manner:

As the frequencies of the atoms are independent of the temperature, the influence of increasing temperature can only become apparent in solid bodies when the amplitudes of the vibrating atoms become considerable. A temperature will ultimately be reached at which neighbouring atoms come into contact at their maximum displacement from the centre of equilibrium. When this occurs, they will no longer return to their original position, and a fixed configuration in space becomes impossible, *i.e.* the solid becomes a liquid. The melting point is, therefore, the temperature at which the amplitude of vibration of the atoms is equal to the mean distance between them. From this hypothesis, Lindemann deduces the formula,

$$\nu = k\sqrt{\frac{T_s}{M.V^{\frac{2}{3}}}},$$

in which T_s is the melting point on the absolute scale, M is the atomic weight, and V is the atomic volume at the melting point. Comparing the values of ν deduced from the measurements of the specific heats with those calculated from the above formula, we obtain for k the value $2{\cdot}8 \times 10^{12}$. The following table† enables us to compare the values of ν calculated in various ways.

* *Phys. Zeitschr.* **11**, 609 (1910).

† See Eucken, *Jahrb. der Radioaktivitat*, **8**, 489 (1912).

The figures in column (i) are calculated from optical measurements, those in (ii) from the specific heat, and those in (iii) from the melting point and the atomic volume.

	(i)		(ii)	(iii)
Al - - -	—		$8{\cdot}3 \cdot 10^{12}$	$7{\cdot}6 \cdot 10^{12}$
Cu - - -	—		$6{\cdot}6 \cdot 10^{12}$	$6{\cdot}8 \cdot 10^{12}$
Zn - - -	—		$4{\cdot}8 \cdot 10^{12}$	$4{\cdot}4 \cdot 10^{12}$
Ag - - -	—		$4{\cdot}5 \cdot 10^{12}$	$4{\cdot}4 \cdot 10^{12}$
Pb - - -	—		$1{\cdot}9 \cdot 10^{12}$	$1{\cdot}8 \cdot 10^{12}$
Diamond - -	—		$40{\cdot}0 \cdot 10^{12}$	$32{\cdot}5 \cdot 10^{12}$
NaCl - - -	$5{\cdot}6$	$6{\cdot}4 \cdot 10^{12}$	$6{\cdot}0 \cdot 10^{12}$	$7{\cdot}2 \cdot 10^{12}$
KCl - - -	$4{\cdot}3$	$4{\cdot}8 \cdot 10^{12}$	$4{\cdot}5 \cdot 10^{12}$	$5{\cdot}6 \cdot 10^{12}$
KBr - - -	$3{\cdot}5$	$4{\cdot}0 \cdot 10^{12}$	$3{\cdot}7 \cdot 10^{12}$	$4{\cdot}2 \cdot 10^{12}$

The agreement is remarkable.

The expansion of solid bodies. All solid bodies expand when their temperature is raised. If l_1 is the length of a rod of the substance at the temperature t_1, and l_2 the length at the temperature t_2, then the quantity

$$\alpha = \frac{l_2 - l_1}{(t_2 - t_1) l_1},$$

which is always positive, is called the coefficient of linear expansion, or more strictly the "mean" coefficient of linear expansion between the temperatures t_2 and t_1. For example, the length of a rod of iron at 0° C. was found to be $l_1 = 2m$, and at 100° its length was $l_2 = 2{\cdot}0024m$. The mean coefficient of linear expansion of iron between 0° and 100° is therefore

$$\alpha = \frac{2{\cdot}0024 - 2}{2 \times 100} = 0{\cdot}000012.$$

For many substances this quantity is very nearly independent of the temperature and of the magnitude of the interval $t_2 - t_1$, so that the relative expansion per 1° C., viz. $\frac{l_2 - l_1}{l_1(t_2 - t_1)}$, is constant for a considerable range of temperature. In this case, we may represent the length of the rod by the linear equation

$$l = l_0(1 + \alpha t).$$

In many cases, the expansion does not follow this simple law. We must then have recourse to the more general equation

$$l = l_0(1 + a_1 t + a_2 t^2 + a_3 t^3 + \ldots).$$

The quantity $\frac{l_2 - l_1}{l_1(t_2 - t_1)}$ is then itself a function of the temperature, and the length of the rod increases by unequal amounts per 1° C. as we raise the temperature. If we wish to determine the true coefficient of expansion at the temperature t, we must measure the small increase in length, which corresponds to a rise in temperature from t to $t + dt$. The smaller we take dt, the closer will be the approximation to the true coefficient of expansion, so that we may write $\alpha = \frac{dl}{dt}$ $\left(\frac{dl}{dt}\right.$ is the differential coefficient of l with respect to $\left.t\right)$. The true coefficient of expansion cannot be determined directly, but it can be calculated with the aid of the differential calculus from the mean coefficient of expansion, much as the true specific heat was calculated from the mean specific heat on page 23. In the general case, mentioned above, the true coefficient of expansion at the temperature t is

$$\alpha = a_1 + 2a_2 t + 3a_3 t^2 + \ldots.$$

The expansion on heating is not confined merely to the length of the solid body, but increases all the dimensions (of an isotropic body) uniformly. In the simplest case, we have for the length l, the breadth b, and the height c of a rectangular parallelepiped the equations:

$$l = l_0(1 + \alpha t),$$
$$b = b_0(1 + \alpha t),$$
$$c = c_0(1 + \alpha t);$$

and for the volume V at the temperature t:

$$V = l \,.\, b \,.\, c = l_0 b_0 c_0 (1 + \alpha t)^3 = l_0 b_0 c_0 (1 + 3\alpha t + 3\alpha^2 t^2 + \alpha^3 t^3).$$

As α is always a very small quantity, we may neglect higher powers of α than the first, and obtain as a first approximation to the volume of the solid body

$$V = V_0(1 + 3\alpha t).$$

The quantity 3α is called the coefficient of cubical expansion, which is, therefore, three times as great as the coefficient of

linear expansion. This relationship between the linear and the cubical coefficients of expansion does not hold, however, for certain crystals which do not belong to the regular system. In such anisotropic bodies the coefficient of linear expansion may be different in all three directions of space. As a consequence of this unequal expansion the angles between the faces of the crystal are altered by heating. Thus the obtuse angle of a calcite rhombohedron is diminished by 8·5 minutes on raising the temperature to 100°. According to Mitscherlich, calcite expands in the direction of the optical axis, but contracts in a direction at right angles to it.

The value of the coefficient of expansion is characteristic of the substance. It has not yet been found possible to connect this quantity with chemical properties, such as the atomic weight of elements, or the molecular weight of compounds.

The coefficient of expansion generally increases, if it varies at all, with the temperature, but by amounts which vary for different substances. It would not be worth while to discuss the numerical data here, but we may mention that there appears to be a distinct parallelism between the coefficient of expansion and the specific heat.* The experimental methods of determining the coefficient of expansion will be found in most text-books on physics.

3. Transition from the solid to the liquid state (fusion).

When a solid body is made to absorb heat, we have seen that its temperature, and its volume, and hence also its specific gravity, are all altered. At the same time, a great number of the other physical properties of the body are changed; for example, its optical properties (refractive index and reflectivity), its electrical and thermal conductivity, etc. All these properties vary continuously with the temperature, so that we have a continuously changing series of intermediate states of the body between any two temperatures. There is a temperature for every body at which this continuous change of the physical properties ceases, viz. the temperature at which the body changes from the solid to the liquid state. This process

*See Lindemann, *Phys. Zeit.* **12**, 1197 (1911).

is known as fusion, and the temperature at which it takes place is called the melting point of the body.

The melting point—apart from a very slight variation with the pressure—is a definite and unique temperature for every pure substance.

There are one or two exceptions to this rule, however, such as glass and pitch. These substances remain soft for a considerable interval of temperature, becoming less and less viscous as the temperature rises, until they ultimately liquefy. This property is peculiar to so-called amorphous, *i.e.* non-crystalline, bodies. We shall exclude bodies of this kind from consideration, and also liquid crystals and crystalline fluids, substances which appear to combine the characteristic properties of the solid and of the liquid states. They have the fixed configuration of the molecules in space peculiar to solids, as well as the mobility of liquids. The transition from an anisotropic crystal to a perfectly isotropic fluid always takes place at one definite temperature. The softening of crystals in the neighbourhood of the melting point is not an exception to this rule, since these softened crystals are still anisotropic.

The transition from the solid state to the liquid state is always accompanied by the absorption of heat. A definite amount of heat, which is called the latent heat of fusion, is absorbed when unit mass of a solid body melts. The latent heat of water, for example, is 80 cal., that is to say, when 1 gr. of ice melts to form 1 gr. of water at 0°, the heat absorbed would heat 1 gr. of water from 0° to 80°. In consequence of the absorption of heat on melting, the temperature of a solid body cannot be raised above its melting point. The heat which we make the body absorb after it has reached the melting point can no longer raise the temperature, as it is all used up in the process of fusion. Only when the whole of the solid has melted does a further addition of heat cause the temperature of the liquid to rise. A mixture of solid and liquid remains permanently at the constant temperature of the melting point.

This fact is made use of in the determination of the melting point. If we immerse a thermometer in a sufficient quantity of a solid, or melted substance, and take care, by means of

efficient stirring, that the solid and liquid are in intimate contact, we can determine the melting point by noting the temperature at which neither absorption nor abstraction of heat produces any change in the thermometer reading. If we have only small quantities of the substance at our disposal, it is best to introduce portions in the form of powder into a fine capillary tube closed at one end. The capillary is then submerged in a bath of a transparent liquid (such as water, sulphuric acid, or glycerine), and is slowly heated. The temperature at which the substance begins to melt is read on a thermometer. The bulb of the thermometer should be placed as close to the capillary as possible.

For metals of high melting point, Holborn and Day recommend the following procedure:* A wire of the metal about 1 cm. in length is placed at the junction of a thermocouple, and the electromotive force is measured as soon as the wire melts. In certain cases precautions must be taken to prevent chemical action with the atmospheric air. The table on page 44 gives the melting point t_0, and the latent heat of fusion w of the more important elements.

There is a distinct connection between the atomic weight and the melting point of elements in the various groups of the periodic system. For example, the melting point decreases in the group Li, Na, K, Rb, Cs, and also in the group Cd, Zn, Hg. In other cases this rule does not hold, as in the group Cu, Ag, Au. There is clearly no universal relationship between melting point and atomic weight, or position in the periodic system. There is apparently just as little connection between the melting point of a compound and the melting point of its components. The only element of which we do not know the melting point is carbon. Even at the highest temperatures carbon has not been obtained in the liquid state. On the other hand, evaporation, *i.e.* conversion into gas (sublimation), has been observed. On account of this tendency of carbon to evaporate at temperatures below the melting point, the determination of the melting point will only be possible at a very high pressure.

The latent heat of fusion can be determined by any of the calorimetrical methods described above. It has a definite value

* *Ann. d. Physik*, (4), **2**, 505 (1900).

	t_0*	w	$A.w$	$\frac{A.w}{273+t_0}$
Aluminium	657°	239·4	6470	6·74
Antimony	630	—	—	—
Argon	−188	—	—	—
Barium	850	—	—	—
Lead	327	5·37	1100	1·8
Bromine	−7·3	16·2	1259	4·7
Cadmium	321·7	13·7	1435	2·4
Caesium	28	—	—	—
Calcium	800	—	—	—
Chlorine	−102	—	—	—
Chromium	1550	—	—	—
Iron (γ)	1530	6·0	336	0·2
Fluorine	−233	—	—	—
Gold	1062	—	—	—
Iodine	113	11·7	1480	—
Potassium	62	13·6	531	3·8
Copper	1083	41·6	2760	1·6
Lithium	179	—	—	2·6
Magnesium	650	—	—	—
Manganese	1228	—	—	—
Sodium	97·5	17·75	409	1·1
Nickel	1451	4·6	270	0·15
Palladium	1549	36	3840	0·46
Phosphorus	44	4·75	147	2·1
Platinum	1755	27·2	5300	2·6
Mercury	−39	2·82	565	2·4
Rubidium	38·5	—	—	—
Oxygen	−227	—	—	—
Sulphur (monoclinic)	119	9·4	301	0·8
Silver	961	21·1	2280	1·85
Nitrogen	−210	—	—	—
Hydrogen	−259	—	—	—
Bismuth	271	12·4	2600	4·8
Zinc	419	28·1	1840	2·3
Tin	232	14·0	1650	3·3

for each substance, but there is no simple relationship between the latent heat and the atomic, or the molecular weight. Walden has shown† that the expression $\frac{M.w}{273+T_0}$ is a constant, viz.

* From Landolt-Börnstein, 4th edition.

† *Zeit. f. Elektrochemie*, **14**, 713 (1908).

13·5 approximately, for many compounds. The last column of the above table shows that this relationship is not applicable to the elements.

The increase in the heat content of a solid body on raising the temperature is accompanied by a continuous change in its physical properties, but when we come to the melting point a further absorption of heat produces an abrupt change in these properties.

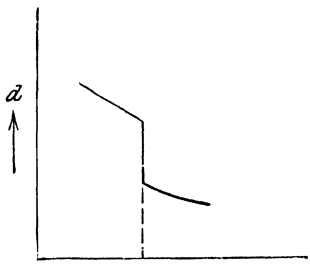


Fig. 9.

The specific heat of most substances increases on melting; the specific gravity, on the other hand, generally decreases. Melting, therefore, is generally accompanied by an increase in the volume of unit mass. Only in a few cases, such as water, cast iron, bismuth, and potassium nitrate, does contraction take place on melting. If we plot the specific gravities of a substance as ordinates, and its temperatures as abscissae, we obtain a curve of the form shown in Fig. 9. A very simple and convenient apparatus for determining this change in volume is shown in Fig. 10. The black portions of the diagram represent mercury, which is forced out at *b*, and weighed if the change in volume is sufficiently great. If the expansion is too small for this method, the tap *b* is closed, and the movement of the mercury through the tap *c* is read off on the scale *r*. The table on page 46 gives the specific heat and the specific gravity of several bodies in the solid and liquid states, and the change on melting Δ, calculated in per cent. of the values characteristic of the solid state.

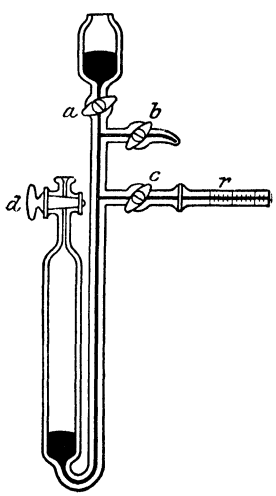


Fig. 10.

Substance.	d_{solid}	$d_{liq.}$	Δ%	c_{solid}	c_{liq}	Δ%
Lead - -	11·005	10·645	−3·39	0·030	0·04	+33
Cadmium -	8·4665	−7·989	−4·72	—	—	—
Tin - -	7·1835	·988	−2·80	0·055	0·0635	+15·6
Mercury -	14·193	13·690	−3·67	0·032	0·0335	+4·8
Bismuth -	9·637	10·004	+3·31	0·030	0·036	+20
Water - -	0·91666	0·99988	+9·1	0·50	1·0	100
Potassium Nitrate -	—	—	—	0·124	0·33	166*

The conductivity for heat and electricity, and also the optical constants, change suddenly at the melting point.

The melting point is the only temperature at which both solid and liquid states of a body can exist permanently in contact with one another. When a liquid is cooled below its melting point, we should expect it to become solid. Often, however, the solidification does not take place. Many melted substances can be "super-cooled," often to the extent of several degrees, if the liquid is pure, and is protected from mechanical shock. If, however, we introduce a small nucleus of the solid substances into the "super-cooled" liquid, solidification begins at once. At the same time, the latent heat of fusion, which is set free during the solidification, causes the temperature of the mixtures of solid and liquid to rise until the melting point is reached. While this "super-cooling" of liquids is very easy to produce, a corresponding super-heating of solid bodies has very rarely been observed.

4. The liquid state.

Specific heat. The specific heat of liquids does not invariably rise with the temperature. The variation with the temperature is generally greater in the liquid than in the solid state, but it occasionally happens that the specific heat of a substance rises at one temperature and falls at another. The best example of this is water, which is abnormal in many ways, and occupies a unique position amongst liquids. According to the measure-

* Recently some very accurate determinations of the change in volume on melting have been made by H. Block, *Zeit. f. physik. Chem.* **78**, 385 (1912).

ments and calculations of Dieterici,* the mean specific heat c_m between 0 and t, and the true specific heat c_w at the temperature t are as follows :

(The mean specific heat of water between 0 and 100 is taken as 1.)

t	c_m	c_w	t	c_m	c_w
0	1·0075	1·0075	70	0·9980	1·0012
5	1·0057	1·0037	80	0·9985	1·0032
10	1·0040	1·0008	90	0·9992	1·0057
15	1·0025	0·9987	100	1·000	1·0086
20	1·0010	0·9974	140	1·0046	1·0244
25	0·9996	0·9970	180	1·0113	1·0468
30	0·9984	0·9971	200	1·0155	1·0605
40	0·9973	0·9974	240	1·0256	1·0928
50	0·9974	0·9983	280	1·0380	1·1318
60	0·9976	0·9995	300	1·0449	1·1538

According to this table, the mean specific heat has a minimum at 37·5, and the true specific heat has a minimum at 25°. The specific heat of mercury decreases steadily, as the temperature rises, according to the linear equation :

$$c_w = 0{\cdot}03336 - 0{\cdot}0000069t.$$

The specific heat of most other liquids, like that of solids, rises with the temperature.

The following table shows the variation of the specific heat with temperature for a few liquids :

Methylalcohol †	$c_m = 0{\cdot}5634 + 0{\cdot}002715t - 0{\cdot}0000376t^2$.
Ethylalcohol †	$c_w = 0{\cdot}5396 + 0{\cdot}001698t$.
Propylalcohol †	$c_w = 0{\cdot}5279 + 0{\cdot}001692t$.
Ether ‡	$c_m = 0{\cdot}52901 + 0{\cdot}0002958t$.
Chloroform ‡	$c_m = 0{\cdot}23235 + 0{\cdot}0000507t$.
Turpentine ‡	$c_m = 0{\cdot}41058 + 0{\cdot}0006193t - 0{\cdot}000001327t^2$.

The specific heat of some liquids appears to decrease towards a lower limit between 0° and −100°.§

* *Ann. d. Physik.* (4), **16**, 593 (1905).

† Bose, *Zeit. f. physik. Chem.* **58**, 585 (1907).

‡ Regnault, quoted from Winkelmann, *Handbuch*, iii. p. 196.

§ Batelli, *Phys. Zeit.* **9**, 671 (1908).

The specific heat of mixtures of liquids can rarely be calculated additively from the specific heats of the components. There is generally a considerable deviation from the law of mixtures, and the calculated value is always larger than one would expect. Mixtures of liquids which are closely related chemically, such as ethyl and methyl alcohol,* chloroform and carbon disulphide, behave normally; mixtures of water with alcohol, or of alcohol with other organic liquids, show large deviations. It is noteworthy that heat is evolved on mixing these liquids, an indication that chemical combination also is taking place. This is probably the reason for the alteration in the heat capacity, since the specific heat of liquid chemical compounds cannot be calculated additively from the specific heats of the components. The regularities shown by solid bodies do not hold even approximately for liquids.

The specific heat of aqueous solutions is always considerably smaller than would be demanded by the law of mixtures. The decrease of the capacity for heat, consequent on solution, is often so great that the heat capacity of the solution is actually smaller than that of the water which it contains. The formation of aqueous solutions is accompanied by absorption of heat, in contra-distinction to the behaviour of the mixtures of liquids which we have just mentioned. There would appear, therefore, to be some connection between the change in the capacity for heat and the heat which is evolved or absorbed on mixing, so far, at least, as the sign is concerned. The heat capacity of many solutions is approximately equal to that of the water which they contain. As far as the specific heat and specific volume of aqueous solutions is concerned, we might compare them to pure water under a high pressure.†

Expansion of liquids on heating. The definition of the coefficient of expansion of a liquid is identical with that of the coefficient of cubical expansion of a solid substance. There are two important methods of measuring the coefficient of

* Bose, *l.c.*

† Cf. in particular Tammann, *Die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen.* Hamburg, 1907.

expansion. The dilatometer which was invented by Kopp consists of a bulb, generally spherical in shape, which contains the liquid, and a calibrated capillary tube in communication with the bulb. When the bulb is heated, the liquid rises in the capillary, and the increase in volume can be calculated from this rise, if the volume of the bulb and the cross section of the capillary are known. It is, of course, necessary to make allowance for the expansion of the glass walls of the bulb. As the coefficient of expansion is much larger for liquids than for solids, this correction is generally very small. The second method is based on the law that liquids in vertical tubes in communication with one another are in equilibrium, when the height of each liquid is inversely proportional to its density. The limbs of a U tube are filled with two non-miscible liquids, one of which has a known coefficient of expansion, and the thermal expansion of the other is measured by comparing the relative heights of the two liquids at different temperatures. This method is independent of the expansion of the walls of the vessel. A third method is to determine the specific gravity of the liquid at various temperatures, and to calculate the expansion from the data thus obtained.

The value of the coefficient of expansion and of its variation with the temperature for liquids, as for solids, is dependent on the substance. No generally valid relationship has yet been found between the coefficient of expansion and the chemical constitution, or the physical properties of a body.

The coefficient of expansion of mercury is constant between 0° and 100°, *i.e.* it is independent of the temperature. This follows from the definition of the centigrade scale, as the total expansion of mercury between 0° and 100° was divided into 100 equal parts. If the mercury thermometer were used for the definition of higher temperatures, the coefficient of expansion of mercury would necessarily be constant for these temperatures also. As the gas thermometer is used for the measurement of high temperatures, and as the mercury thermometer gives slightly different readings from the gas thermometer, even at 200° (see p. 8), the coefficient of expansion of mercury must vary slightly with the temperature measured in this way. The most accurate

measurements of the mean coefficient of expansion of mercury are as follows: *

Between	0°	and	100°	0·00018092.
,,	0°	,,	200°	0·00018094.
,,	0°	,,	300°	0·00018129.

Water and aqueous solutions behave quite exceptionally. When water at the melting point is heated it first contracts until the density reaches a maximum at about 4°. Above this temperature, its density, like that of other liquids, diminishes continuously with the temperature. A very original method of determining this temperature of maximum density accurately was first employed by Rumford in 1805, and has been used since then by other investigators. The method consists in the observation of two or more thermometers placed vertically one over the other in a vessel filled with water. The temperature of the water at the beginning is above 4°, and is allowed to fall gradually by placing the vessel in cooler surroundings. As the lighter water rises to the surface, the uppermost thermometer will register the highest temperature so long as the warmer water is the less dense. At the temperature of maximum density all thermometers must register the same temperature. At temperatures below this, the uppermost thermometer will register the lowest temperature. According to the latest determinations, the most probable value of the temperature of maximum density is 3·972°. When water is compressed, the temperature of maximum density is lowered. According to experiments made by Lussanna† it is

3·2°	at	41·6 Atm.
2·0°	,,	93·3 ,,
0·8°	,,	144·8 ,,

To explain the abnormal behaviour of water, we assume that the water molecules polymerise more and more as the temperature falls, according to the equation

$$n\mathrm{H_2O} = (\mathrm{H_2O})_n.$$

The polymerised molecules occupy more space than the n simple molecules. A rise in temperature has thus an effect in two

* Landolt-Börnstein, 4th ed. Cf. also the paper by Callendar and Mors, *Proc. Roy. Soc.* London, A. **84**, 595 (1911).

† Quoted from Winkelmann, *Handbuch*, iii. p. 90.

different directions: (1) an increase in volume consequent on the ordinary thermal expansion, and (2) a diminution in volume consequent on the splitting up of the polymerised molecules. Below the temperature of maximum density the second effect is predominant, above 4° the first.

All aqueous solutions have maxima of density, which occur at temperatures lower than 4°. The temperature of maximum density is lowered like the freezing point when a substance is dissolved in water, but to a much greater degree. According to the investigations of de Coppet,* the lowering of the temperature of maximum density in salt solutions is proportional to their molecular concentration; but the molecular lowering varies for each salt.

The coefficient of expansion of liquids is a more complicated function of the temperature than that of solid bodies. The linear equation is practically never sufficient to represent the temperature variation. In general it is necessary to resort to a three-constant equation:

$$V = V_0(1 + \alpha t + \beta t^2 + \gamma t^3).$$

5. Evaporation.

Every liquid at every temperature has a tendency to become gaseous, *i.e.* to evaporate. This property may also be observed in some solids, but, generally, to such an insignificant degree that we may disregard it. In liquids the tendency is considerably greater, and increases in every case when the temperature is raised.

If we introduce a portion of a liquid into the interior of a closed space, evaporation takes place until the vapour (*i.e.* gas composed of the same molecules as the liquid) has attained a pressure which at every temperature is characteristic of the liquid. The evaporation then ceases; there is equilibrium between the liquid and its vapour. This pressure, which we may look upon as a measure of the tendency to evaporate, is called the vapour pressure. It increases with the temperature for all substances.

The following simple experiment may be used for the demonstration and for the measurement of vapour pressure. A small

* *Compt. rend. de l'Acad. des Sc.* **132**, 1218 (1901).

quantity of a liquid (water, for example) is introduced into the empty space of a Torricellian vacuum (Fig. 11) by means of a pipette. The level of the mercury at once falls. If water at 20° be taken, the mercury falls by 17 mm. The empty space above the mercury is now full of water vapour, and the pressure, which this vapour exerts, is equal to that of a column of mercury 17 mm. high. If we introduce a small quantity of ether instead of water into the barometer tube, the level of the mercury falls by about 440 mm. Ether at 20° has, therefore, a vapour pressure of 440 mm.

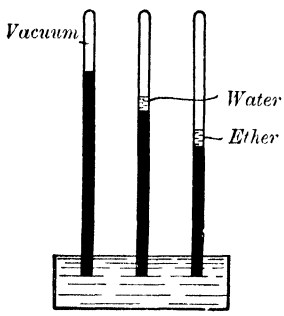


FIG. 11.

When a liquid is left in the open air a layer of vapour forms on its surface, and the partial pressure of this vapour is equal to the vapour pressure of the liquid. By degrees the vapour is distributed by diffusion throughout the whole of the space at its disposal, and the vapour which has diffused away is replaced by further evaporation of the liquid, so that the partial pressure of the vapour at the surface of the liquid remains constant. This process goes on until the whole of the liquid has evaporated.

If the vapour pressure of a liquid is raised by increasing the temperature until it becomes greater than the pressure exerted on the liquid by the atmosphere, the vapour pushes the air away from the surface, and the evaporation proceeds very rapidly; in other words, the liquid boils. The boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid is just greater than that of the surrounding atmosphere, *i.e.* about 760 mm. of mercury under normal conditions. When the barometer is low, as at the top of a high hill, liquids boil at temperatures below their normal boiling point.

Evaporation, *i.e.* the transition from the liquid to the gaseous state, can only take place if the liquid absorbs a definite quantity of heat, which for unit mass, 1 gr., is called the latent heat of evaporation. The evaporation proceeds only so long as the necessary amount of heat is supplied to the liquid. If the

supply of heat is stopped, the latent heat of evaporation is taken from the heat content of the liquid itself. The temperature and with it the vapour pressure diminish in consequence, until the heat, flowing into the liquid from its surroundings, just suffices to compensate for that which is used up in the slow evaporation. If we supply heat to a liquid in an open vessel, the temperature and the vapour pressure rise in the first instance. As long as the vapour pressure is lower than the atmospheric pressure, the evaporation is very slight, and the heat supplied to the liquid is used up mainly in raising the temperature. At the boiling point, however, the whole of the heat supplied to the liquid is employed in the process of evaporation, and the temperature of the liquid remains constant as long as any of the liquid is left. This fact is made use of in the determination of the boiling point.

By super-heating a liquid we mean heating it above its boiling point. Super-heating, like super-cooling (p. 46), takes place when the liquid is pure, and mechanical shock is avoided. A super-heated liquid may evaporate explosively, large bubbles of vapour forming suddenly in the interior of the liquid. Super-heating can be prevented by putting small particles of solid bodies, such as tile chips, or pieces of metal, into the liquid.

According to Trouton, the following relationship exists between the latent heat and the boiling point of liquids. If we take the boiling point, not in degrees centigrade t, but in degrees absolute, $T = t + 273$, then

$$\frac{M \times \lambda}{T_0} = \text{const.} = 21 \text{ (approx.)},$$

where M is the molecular weight of the liquid. For liquids which are more or less polymerised this constant has a higher value, and we might use the deviations from Trouton's rule to determine the extent of the polymerisation. Nernst, however, has shown that this rule only applies to liquids whose boiling points are not very far apart. For liquids of very low boiling point, such as the liquefied permanent gases, the values of the constant are much too small. Nernst gives a formula* which

* *Lehrbuch*, 6th edition, p. 278.

is in closer agreement with experiment, as is shown for a number of substances by the following table. Nernst's equation is:

$$\frac{M \times \lambda}{T_0} = 9{\cdot}5 \log T_0 - 0{\cdot}007 T_0.$$

Substance.	T_0	$M \times \lambda$	$\frac{M \times \lambda}{T_0}$	
			found.	calc.
Hydrogen	20·4	248	12·2	12·3
Nitrogen	77·5	1362	17·6	17·4
Argon	86·0	1460	17·0	17·8
Oxygen	90·6	1664	18·3	18·0
Methane	108	1951	18·0	18·6
Ethyl ether	308	6466	21·1	21·5
Carbon disulphide	319	6490	20·4	21·6
Benzine	353	7497	21·2	21·7
Stannic chloride	387	7960	20·6	21·9
Aniline	457	10500	23·0	22·1
Methyl salicylate	497	11000	22·2	22·1
Mercury	630	12400	19·7	22·2
Sulphur	718	11600	16·2	22·2

Evaporation of a liquid can only take place when the vapour pressure of the liquid is greater than the external pressure to which it is subjected. One might assume from this that the formation of vapour could be prevented at all temperatures by increasing the external pressure sufficiently. As the vapour pressure always rises very rapidly with the temperature, we should no doubt have to exert a very high pressure at temperatures much above the boiling point. Yet we might imagine it to be possible to obtain every substance even at the highest temperatures in the liquid state. This result is not confirmed by experience; there is a temperature for each substance above which it cannot exist in the liquid state, no matter how much we increase the pressure. This temperature is called the critical temperature, or, as it is sometimes termed, the absolute boiling point.

The classical researches of Andrews on carbon dioxide led to the discovery of the critical temperature. If we enclose some liquefied carbon dioxide at 0°, let us say, in a thick-walled

evacuated glass tube, we see a distinct boundary between the heavier liquid and the space above it which is filled with gaseous carbon dioxide. The pressure in this space is the vapour pressure of carbon dioxide at 0°. If we heat the vessel, we notice that the quantity of liquid diminishes, as the vapour pressure rises more rapidly with the temperature than the pressure of the gas would have risen had it been heated by itself. Liquid must consequently evaporate until the pressure in the gaseous portion has become equal to the vapour pressure. As the temperature rises, the density (specific gravity) of the liquid diminishes on account of the expansion. The density of the vapour, on the other hand, increases. Ultimately a temperature is attained at which the density of the liquid and of the vapour become equal to one another, so that the meniscus, the sharp boundary between the liquid and the vapour, disappears. At this critical temperature the liquid and the gaseous states of matter become identical with one another. The critical temperature of carbon dioxide is 31°. The vapour pressure of the liquid at this temperature is called the critical pressure. The volume which unit mass of the substance occupies at its critical temperature and critical pressure is called the critical volume. The density of the substance at the critical temperature and the critical pressure is called the critical density.

No gaseous substance above its critical temperature can be liquefied by compression. On the other hand, it is possible by cooling to convert a gaseous substance into a liquid without any sudden transition from the one state to the other. For example, if we cool carbon dioxide under a pressure of 100 atmospheres at 35° in the glass tube mentioned above to below 31°, let us say to 25°, keeping the pressure constant all the time, we should be unable to observe any change in the tube during cooling. We might be tempted to assume that the carbon dioxide had remained gaseous. It is easy to show that this conclusion is incorrect. If we lower the pressure until it is less than the vapour pressure of carbon dioxide at 25°, we observe the sudden formation of a meniscus, and of a small bubble of vapour above the liquid, a sign that the liquid has begun to

ressure at constant temperature

could produce vapour, but could never produce liquid, the liquid must have been present before we began to diminish the pressure. The transition from gas to liquid by cooling to below the critical temperature at constant pressure has, therefore, taken place continuously.

Every pure substance has a definite critical temperature, critical pressure, and critical density. We shall discuss the relationships between these quantities and the molecular weight in greater detail in a later paragraph. We may mention at this stage that Guldberg found the normal boiling point of all substances to be a nearly constant fraction of their critical temperature measured on the absolute scale. The table on p. 57 shows how far this rule is obeyed.*

6. Gases.

The equation of condition. The expansion of gases on heating is very much greater than that of solid and liquid bodies, and obeys much simpler laws. Gay-Lussac was the first to publish an empirical law which states that all gases expand by the same fraction α of the volume which they occupy at 0° when their temperature is raised 1° C. The value of this fraction α is $\frac{1}{273}$. If the volume of unit mass of the gas at 0° is V_0, its volume at t° is

$$V_t = V_0(1+\alpha t). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This equation holds only when the pressure remains constant during the change in temperature. Gay-Lussac found also that the pressure p of a gas increases by the same fraction α of the pressure at 0° if the volume be kept constant during heating, so that

$$p_t = p_0(1+\alpha t). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

To find the law of expansion under variable pressure, we must combine the above equations with Boyle's law. Boyle's law states that when we compress or dilate a gas at constant temperature, the volume and the pressure are inversely proportional to one another. The product pv, therefore, does not vary, *i.e.*

$$pv = \text{const.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

* Winkelmann, *Handbuch*, **3**. p. 860 *et seq.*

Let unit mass of the gas (1 gr.) at the temperature 0° and the pressure p_0 occupy the volume v_0; we wish to calculate what volume v this quantity of gas will occupy at any temperature t and any pressure p.

Substance.	Critical Temp. t_k	Critical Pressure p_k (Atm.)	Critical Density d_k	Boiling Point t_s	$\frac{t_k+273}{t_s+273}$
Hydrogen	-240·8	14	—	-252·6	0·634
Nitrogen	-146	35	0·44	-195·5	0·610
Argon	-121	50·6	—	-187	0·567
Oxygen	-118	50	0·60	-182·4	0·567
Methane	-95·5	50	—	-165	0·623
Ethylene	10·1	51	0·21	-103	0·600
Carbon dioxide	31·35	72·9	0·464	—	
Nitrous oxide	35·4	75·5	0·454	-89·8	0·594
Hydrogen chloride	51·5	86	0·61	-83·7	0·583
Hydrogen sulphide	100	92		-61·6	0·566
Ammonia	130	115·0		-33·5	0·595
Chlorine	141	84		-37·6	0·569
Sulphur dioxide	155·4	79	0·49	-10	0·613
Ether	194·4	35·6	0·263	35	0·659
Chloroform	260	55		60	0·615
Carbon disulphide	272	74	0·377	46	0·585
Benzene	288·5	47·9	0·304	80	0·625
Water	364·3	194·6	0·208	100	0·580
Stannic chloride	319	40	0·742	114	0·653
Aniline	426	52·4	—	184	0·572
				Mean ca.	0·6

If we raise the temperature to $t°$ at the constant pressure p_0, the volume increases to $v' = v_0(1+\alpha t)$. If we compress (or dilate) the gas at the constant temperature t until the pressure has become equal to p, the volume diminishes (or increases) to the value v, where $pv = p_0 v'$ by equation (3). Between the initial values p_0, v_0, 0, and the final values p, v, t, we derive from this the equation

$$pv = p_0 v_0(1+\alpha t). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The pressure, the volume, and the temperature of a gas are connected with one another in all cases by equation (4). α is

a constant for all gases, and is very nearly equal to $\frac{1}{273}$.* The product p_0v_0 has a different value for each gas. If we know this value and two of the quantities p, v, t, we can calculate the third from equation (4).

Equation (4) may be obtained in a more general form by comparing the gr. molecular volumes, *i.e.* the volumes which are occupied by the gr. molecular weight of the various gases, instead of the volumes of unit mass. Experiment has shown that all gases under the same conditions of pressure and temperature have the same molecular volume, which is explained by the hypothesis of Avogadro, that equal volumes of all gases contain the same number of molecules. As the molecular volume v_0 at the pressure p_0 and temperature 0° has the same value for all gases, equation (4*a*),

$$pv = p_0v_0(1 + \alpha t),$$

is independent of the nature of the gas. It will hold for all gases if we take v as the volume of the gr. molecular weight (1 mol.) of the gas.

Equation (4*a*) is simplified still further by the introduction of the conception of absolute temperature. If we extrapolate equation (1) for negative Celsius temperatures, we ultimately arrive at a temperature $t = -\frac{1}{\alpha} = -273$, at which the gas would have contracted so far that its volume would have become 0. This temperature is called the absolute zero, and is taken as the starting point of the absolute scale of temperature. The absolute temperature T differs by the amount $\frac{1}{\alpha} = 273$ from the temperature on the Celsius scale. We have, therefore, for any temperature,

$$T = \frac{1}{\alpha} + t = 273 + t.$$

Substituting this value in equation (4*a*) we obtain

$$pv = p_0v_0\alpha \times T.$$

* D. Berthelot in 1907 gives its value as $\frac{1}{273 \cdot 09}$. According to the latest calculations of Amagat, α is almost exactly $\frac{1}{273 \cdot 000}$ for very rarefied gases. (*C. r. de l'Acad. des Sciences*, **153**, 851 (1911).)

$p_0 v_0 \alpha$ is now a universal constant for all gases, and we shall designate it by the single letter R. We have now for all gases the universally valid equation

$$pv = RT. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4b)$$

An equation of this sort which connects the pressure, the volume, and the temperature of a body with one another is called an "equation of condition." The state of a body is determined uniquely when the values of any two of these quantities are given; for example, p and v, or p and T, or v and T. We may call the three quantities p, v, and T the characteristic variables of the body, or the variables of condition.

The numerical value of the "Gas constant" R depends on the units in which we measure the pressure p and the volume v. If we choose atmospheres and litres as our units, we obtain

$$R = p_0 v_0 \alpha = \frac{1 \times 22{\cdot}4}{273} = 0{\cdot}082,$$

as 1 gr. molecule or 1 mol. of a gas at 0° and 1 atmosphere pressure occupies 22·4 litres. In the absolute system (centimetre-gramme-second system) we have 1 litre = 1000 c.c., and 1 atmosphere = the weight of a column of mercury 76 cm. high, and 1 sq. cm. in cross section, so that $v_0 = 1000 \times 22{\cdot}4$, and

$$p_0 = 76 \times 13{\cdot}6 \times 981,$$

and hence $R = 8{\cdot}32 \times 10^7$. The choice of the absolute zero as $-273°$ C. is important theoretically, but has no significance from a practical point of view. It is impossible to attain to a temperature at which a substance occupies no volume. From this it follows that the laws of Boyle and Gay-Lussac cannot hold for very low temperatures.

Even at moderate and high temperatures these laws are not strictly obeyed. All gases, especially at high pressures and low temperatures, show more or less marked deviations from equation (4*b*). A gas which would obey the equation with absolute accuracy is called "an ideal gas." For real gases the equation can only be regarded as an approximation, although often a

very good one, to the facts. It was not until considerable progress had been made in the experimental methods that these deviations from the formula were detected. The behaviour of real gases has been very carefully investigated, more especially by Amagat and Regnault. Amagat subjected a number of gases at constant temperature to the pressure of a column of mercury many metres in height which he erected in a shaft 400 metres deep. The values of the product pv, which he obtained, are given in the units which he used in the following table :

P (mHg).	Air.	Oxygen.	Hydrogen.	Carbonic Oxide.	Methane.	Ethylene.
24·1	26968	26843	27318	27147	26325	21473
34·9	26908	26614	27618	27102	25596	18352
45·2	26791	—	27652	27007	24998	12263
55·5	26789	26185	27960	27025	24433	9772
64·0	26778	26050	28129	27060	24074	9370
72·2	26792	25858	28323	27071	23724	9703
84·2	26840	25745	28533	27158	23318	10675
101·5	27041	25639	—	27420	22951	12210
133·9	27608	25671	29804	28092	22915	15116
177·6	28540	25891	30755	29217	23739	18962
214·5	29585	26536	31625	30467	25054	22115
250·2	30572	—	32426	31722	26742	25065
303·0	—	28756	—	—	—	29333
304·0	32488	—	33887	33919	29289	—

We see that all gases show considerable deviations from the behaviour of the ideal gas at higher pressures. At lower pressures the deviations are smaller, but can be detected by accurate measurement in all cases. As Regnault has shown, all gases approach more nearly to the ideal condition as the pressure diminishes, or as the dilution increases, so that we may assume that Boyle's law would hold exactly for matter in a very rarefied condition.

The behaviour of real gases is most easily characterised by comparing the values of the products pv at constant temperatures and varying pressures. If we plot the values of p as abscissae and the corresponding values of pv at constant temperature as ordinates, the pv curves for an ideal gas should all be straight lines parallel to the axis of abscissae. As we have

stated, this is never the case for a real gas, and the pv curves, which are generally called isothermals, begin to show a distinct slope even at pressures below 1 atmosphere. If the simple gas laws hold strictly for very small pressures, ($p = 0$), the isothermals of all gases should cut in one and the same point. D. Berthelot has performed this extrapolation,* and obtains for the products pv for 1 gr. molecule of gas the following values at 0° C. The pressure is measured in atmospheres, and the volume in litres.

Hydrogen	22·4187
Carbonic oxide	22·4084
Oxygen	22·4140
Carbon dioxide	22·4146
Acetylene	22·4109
Hydrogen chloride	22·3983
Sulphur dioxide	22·4174
Mean	22·412

The deviations from the mean value 22·412 are very insignificant, and are probably due to unavoidable experimental errors, above all to the uncertainty in the molecular weight on which the calculation of pv is based. For this reason it has been suggested of late to use the values of pv at zero pressure for the determination of the molecular weights of gases. If pv' is the limiting value of pv for 1 gr. of the gas, and M its molecular weight, we may calculate M from the equation $M = \frac{22{\cdot}412}{pv'}$. In this way the atomic weight of nitrogen was found to be 14·01. 14·04, the value which was universally accepted formerly, was determined gravimetrically by Stas, and is certainly incorrect. The isothermals of hydrogen and helium rise upwards with increasing pressure ; those of all other gases, on the other hand, diminish at low pressures, pass through a minimum, and rise again at higher pressures. When the product pv rises with the pressure, the diminution in volume consequent on an increase of pressure is smaller than one would expect it to be, according to Boyle's law. If the values of pv diminish, the gas will contract more on compression than we should expect. Hydrogen and helium are, therefore, less compressible at all pressures than

* *Zeit. f. Elektrochemie*, **10**, 621 (1904).

the ideal gas. All other gases, on the other hand, become more compressible than the ideal gas at low pressures. The compressibility corresponds exactly to Boyle's law at the pressure at which the isothermal passes through a minimum.

These considerations apply only to room temperatures, or to temperatures not far removed from room temperatures. It is probable that all gases will behave like hydrogen and helium at high temperatures, *i.e.* they will all be less compressible at all pressures than Boyle's law demands. On the other hand, it is probable that hydrogen and helium will show the same change in compressibility at very low temperatures as the other gases at the ordinary temperature. Witkowski has shown that pv for hydrogen decreases with the pressure at very low temperatures.* As the law of Boyle and Gay-Lussac does not account exactly for the behaviour of gases, a large number of attempts have been made to find another equation, which should give the relationship between the volume, the temperature, and the pressure of gases more accurately. So far, however, no law has been discovered which is valid, even to a moderate degree of approximation, for all substances at all temperatures and pressures. The most successful step in this direction was made by Van der Waals. A brief discussion of his well-known equation will be given in the following.

We shall show in Chapter IV. that the kinetic theory of gases can account for the behaviour of ideal gases, and that it enables us to deduce the law of Boyle and Gay-Lussac. In the kinetic theory we assume that the molecules of the gas move in straight lines until they are diverted from their course by collisions with other molecules, or with the walls of the enclosing vessel. In order to deduce the simple gas laws it is necessary to assume that the mean distance between the molecules is great compared with the dimensions of a molecule, and that the molecules exert no force on one another, unless the distance separating them is very small. As these conditions are more likely to be complied with at great dilutions, we see that the theory gives a plausible explanation of the exact validity of the simple laws for very rarefied gases. If the mean distance between the molecules is

* *Krak. Anz.* **1905,** 305.

diminished by compression, the volume occupied by the molecules themselves will no longer be negligible in comparison with the whole space at their disposal, and the gas will behave as if it were confined to a smaller space than that which it appears to occupy. In addition, forces of attraction between the molecules come into play, becoming more powerful, and opposing the tendency of the gas to expand more effectively, the more the volume is diminished. To allow for this molecular contraction, a term must be added to p, the pressure which is exerted on the gas. Following up this idea, Van der Waals arrived at the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

The constants a and b, which to a first approximation are independent of the pressure, temperature, and volume, are measures, a of the molecular attraction and b of the dimensions of the molecules.* They vary from gas to gas. At very great dilutions $\frac{a}{v^2}$ is very small, and v is very great compared with b; Van der Waals' equation then becomes identical with the simple equation $pv = RT$.

Van der Waals' equation has been confirmed by experiment in many cases. We can find values of a and b for most gases at not too high pressures, which, substituted in the equation, enable us to calculate the influence of the pressure and the temperature on the volume. The values of the constants increase with the molecular weight, as one might expect. From this it follows that simple gases of low molecular weight, such as the mon-atomic inert gases, the simple diatomic gases, hydrogen, oxygen, nitrogen, carbonic oxide, hydrogen chloride, etc., will approach more closely to the ideal gas in their behaviour. Some values of a and b are given in the following table.† In calculating them the pressure was measured in atmospheres, and the gram-molecular volume in cubic centimetres. b must be multiplied by 10^{-3} and a by 10^{-6}, if the volume is measured in litres.

* b is four times the space actually occupied by the molecules themselves.

† *Zeit. f. physik. Chemie*, **69**, 52 (1910).

	Formula.	b	a
Hydrogen	H_2	23	$0{\cdot}19\times10^6$
Oxygen	O_2	31·6	$1{\cdot}36\times10^6$
Nitrogen	N_2	37·3	$1{\cdot}31\times10^6$
Carbon dioxide	CO_2	42·8	$3{\cdot}61\times10^6$
Carbonic oxide	CO	38·6	$1{\cdot}43\times10^6$
Sulphur dioxide	SO_2	56·5	$6{\cdot}69\times10^6$
Ethane	C_2H_6	69·9	$6{\cdot}0\times10^6$
Pentane	C_5H_{12}	146·4	$19{\cdot}1\times10^6$
Benzene	C_6H_6	120·3	$18{\cdot}71\times10^6$
Carbon tetrachloride	CCl_4	127·3	$20{\cdot}86\times10^6$
Carbon disulphide	CS_2	77·0	$11{\cdot}60\times10^6$
Ethyl ether	C_4H_{10}	134·7	$17{\cdot}44\times10^6$
Ethyl alcohol	C_2H_5OH	84·5	$15{\cdot}22\times10^6$
Acetic acid	CH_3COOH	106·9	$17{\cdot}60\times10^6$
Ethyl acetate	$CH_3COOC_2H_5$	141·3	$20{\cdot}47\times10^6$
Ammonia	NH_3	36·4	$4{\cdot}05\times10^6$
Aniline	$C_6H_5NH_2$	137·0	$26{\cdot}6\times10^6$
Hydrogen chloride	HCl	40·9	$3{\cdot}81\times10^6$
Chlorine	Cl_2	46·1	$5{\cdot}35\times10^6$
Water	H_2O	33·2	$5{\cdot}87\times10^6$
Stannic chloride	$SnCl_4$	164·3	$26{\cdot}94\times10^6$

E. and N. Bose have pointed out that the mass attraction a depends not only on the size of the molecules but also on their constitution. Molecules composed of many atoms exert a greater attraction on one another than molecules of the same mass composed of fewer atoms. For example, the values of a for ethane ($M=30$) in the table is greater than that for oxygen ($M=32$), viz. $6{\cdot}0\times10^6$ as against $1{\cdot}36\times10^6$.

A very important point with regard to Van der Waals' equation is its application to the liquid as well as to the gaseous state. It is clear from the form of the equation that for small values of v, *i.e.* for large values of $\frac{a}{v^2}$, an increment of pressure will only produce a very small diminution in volume, since $\frac{a}{v^2}$ ultimately becomes much greater than p. For small specific volumes, especially if the molecular attraction a is great, the substance is only very slightly compressible, and has, therefore, one of the properties which we associate with the liquid state. Van der Waals' equation accounts for the continuous transition from

the gaseous to the liquid state, which we discussed above. It is possible, in fact, to calculate the critical constants T_k (critical temperature), p_k (critical pressure), and v_k (critical volume) from the constants a and b of Van der Waals' equation. We arrive at this conclusion by the following considerations. Van der Waals' equation,

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT,$$

is of the third degree in v, and there must, therefore, be three values of v for every value of the temperature and pressure. These three roots of the equation must either all be real, or one of them must be real and the other two complex. In the latter case the real root is the only one which is of practical significance, that is to say, there is only a single volume which satisfies the equation for every temperature and pressure. This is the case when the substance is a gas, and when it is above its critical temperature. Below the critical temperature there are for certain pressures two states which can exist in contact with one another, and for which the volume of unit mass has quite distinct values, viz. liquid, and saturated gas in equilibrium with the liquid. The third state which is demanded by the theory (*i.e.* by the cubical equation) has not been realised by experiment, but the theoretical possibility of it is made clear by the graphical representation in Fig. 12. In this figure the pressures are taken as ordinates, and the corresponding volumes at constant temperature as abscissae. For every temperature there is a corresponding curve, which we shall call an isothermal. At the higher temperatures the isothermal (1) approaches to the rectangular hyperbola demanded by the simple gas laws, at lower temperatures

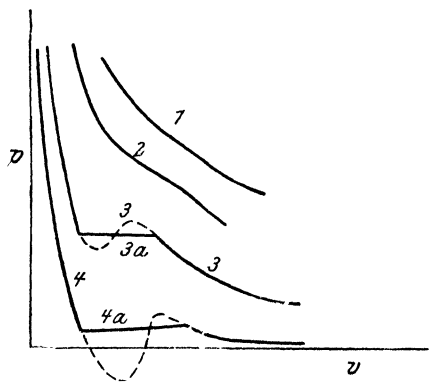


FIG. 12.

(2) considerable deviations begin to appear. For still lower temperatures Van der Waals' equation gives the curves 3 and 4. These have not, however, been confirmed by experiment throughout their whole length. The dotted lines are the parts which have not been realised by experiment. The actual behaviour of the body is represented by the continuous curves $3a$ and $4a$. On raising the pressure at constant temperature, condensation begins to take place as soon as the specific volume corresponding to the saturated vapour has been attained. The volume then diminishes at constant pressure, as the vapour liquefies, until the whole of the vapour has disappeared and only liquid is left. Further increases in pressure produce very slight diminutions in volume owing to the very small compressibility of the liquid. The experimental realisation of the dotted portions of the curves has been attempted in two different ways. By carefully compressing certain vapours at constant temperature it is sometimes possible to continue the compression beyond the condensation point, so that we obtain super-heated vapours. In these cases the volume has been found to vary in accordance with the portion of the dotted curve $3a$ above the horizontal line. The second method is to produce a state of tension (*i.e.* negative pressure) in a liquid, carefully freed from dissolved air, by cooling it in a closed vessel which it fills completely. Liquids may sometimes be subjected to considerable tension in this way before they break away from the walls of the vessel, with formation of vapour. Jul. Meyer has shown recently that the specific volume of liquids subjected to negative pressure in this way follows the dotted curve $4a$.* The beginning and the end of the horizontal straight line correspond to two of the three real roots of the equation at the pressure and temperature which the straight line represents. The third root is the volume corresponding to the intersection of the horizontal straight line and the dotted curve. At the critical point the three roots of the equation become equal to one another. This purely mathematical deduction enables us to calculate the critical values v_k, p_k, T_k from the constants a and b.

* *Zeit. f. Elektrochemie*, **17**, 743 (1911); *Abhandlungen der Bunsengesellschaft*, Nr. 6.

Transforming Van der Waals' equation, and arranging in powers of v, we obtain the equation

$$v^3 - \frac{bp + RT}{p} \cdot v^2 + \frac{a}{p} \cdot v - \frac{ab}{p} = 0.$$

At the critical temperature T_k and the critical pressure p_k, the three roots v_1, v_2, v_3 must all be equal to the critical volume v_k, *i.e.* the equation must be of the form $(v - v_k)^3 = 0$. Equating coefficients, we obtain the three equations:

$$(1) \quad b + \frac{RT_k}{p_k} = 3v_k,$$

$$(2) \quad \frac{a}{p_k} = 3v_k^2,$$

$$(3) \quad \frac{ab}{p_k} = v_k^3,$$

Dividing (3) by (2), we obtain

$$(4) \quad v_k = 3b;$$

from (4) and (2): $$(5) \quad p_k = \frac{a}{27b^2},$$

and from (1), (4), and (5):

$$(6) \quad T_k = \frac{8a}{27bR}.$$

Conversely we can use the equations (4), (5), and (6) to calculate the constants a and b from the critical data. We may use any two of the equations for this calculation, viz. (4) and (5), (4) and (6), or (5) and (6). If Van der Waals' equation were strictly in agreement with experiment, we should obtain identical values for a and b by all three methods. This is not the case, however; there are considerable discrepancies which show that the theory represents the facts only approximately.

Nevertheless, there can be no doubt that the theory gives at least a qualitative picture of the phenomena. We shall mention one other important deduction from it. If we substitute for the coefficients in Van der Waals' equation the values given by (4), (5), and (6),

$$a = 3p_k v_k^2, \quad b = \frac{v_k}{3}, \quad R = \frac{8}{3} \frac{p_k v_k}{T_k},$$

we obtain the equation in form :

$$\left(p+\frac{3p_kv_k^2}{v^2}\right)\times\left(v-\frac{v_k}{3}\right)=\frac{8}{3}\frac{p_kv_k\times T}{T_k},$$

and dividing by $\frac{p_kv_k}{3}$,

$$\left(\frac{p}{p_k}+\frac{3v_k^2}{v^2}\right)\left(3\frac{v}{v_k}-1\right)=8\frac{T}{T_k}.$$

If we put $\frac{p}{p_k}=\pi$, $\frac{v}{v_k}=-\phi$, $\frac{T}{T_k}=\theta$,

i.e. if we reckon pressure, volume, and temperature in fractions of the corresponding critical values, we obtain an equation of condition applicable to all substances, as the constants are all independent of the nature of the substance, namely :

$$\left(\pi+\frac{3}{\phi^2}\right)(3\phi-1)=8\theta.$$

Equation (7) is called the reduced equation of condition, and π, ϕ, and θ are called the reduced variables of condition.

The equation demands that the molecular volumes of all substances at the same reduced temperature and reduced pressure should be the same fraction of their critical volumes. As the equation is intended to apply to all liquid and solid substances, it postulates a very great similarity in the physical behaviour of substances. It is not to be wondered at, therefore, that the theory only gives a very rough picture of the facts. Apart from some marked exceptions, it has been found that the physical properties of various substances may be compared best at equal reduced pressures and temperatures, *i.e.* when the substances are in " corresponding " states.

These relationships are exceedingly important from the point of view of the kinetic theory of matter, but space does not permit of their being discussed here.*

In order to obtain a better agreement with the experimental data, D. Berthelot modified Van der Waals' equation. Instead of equation (7) he proposes the equation

$$\left(\pi+\frac{16}{3}\frac{1}{\theta\phi^2}\right)\left(\phi-\frac{1}{4}\right)=\frac{32}{9}\theta,$$

* Cf. B. Kuenen, *Die Zustandsgleichung*, Samml. Wissenschaft, Brunswick, 1907.

which agrees very well with the observed facts for a considerable interval of temperature and pressure.*

The specific heat of gases. As the density of gases is very small in comparison with that of liquids, accurate determinations of their specific heat can only be made by using very large volumes of gas. Regnault, and others after him, measured the specific heat by leading a constant current of gas from a reservoir at a higher temperature through a water calorimeter and determining the rise in temperature. If we know the mass of gas which has passed through the calorimeter, we can calculate the quantity of heat which unit mass gives out when it is cooled at constant pressure. This method, therefore, gives the quantity c_p for gases. Multiplying c_p by the density, we obtain the specific heat per unit volume. The following table gives one or two of the more important of Regnault's determinations of the mean specific heat c_p between 0 and 100, and shows that for some of the simpler gases the heat capacity of equal volumes is very nearly independent of the nature of the gas.

Mean specific heats, c_p (Regnault), between 0° and 100° C.

Gas.	For 1 g.	For 1 l. (0° 760 mm.).	For 1 mol.
Air - -	0·2375	0·305	
O_2 - -	0·2175	0·31	6·96
N_2 - -	0·2438	0·304	6·83
H_2 -	3·4090	0·304	6·82
CO - -	0·2479	0·309	6·94
Cl_2 - -	0·1214	0·38	8·6
CO_2 - -	0·2025	0·398	8·92
N_2O - -	0·2238	0·44	9·84

Equal volumes of a gas contain the same number of molecules by Avogadro's law, and hence the molecular heat, *i.e.* the quantity of heat necessary to raise the temperature of 1 mol. of the gas by 1°, is a constant for some of the simpler gases. This result was regarded as analogous to the law of Dulong and Petit for the solid elements. Regnault found further that the

* *Mém. et Trav. du Bureau Intern. des Poids et des Mes.* 1907.

molecular heat of a gas is unchanged by variation in pressure between 1 and 12 atmospheres. Later experiments by Lussana show that this law is only approximately true, and that c_p shows a distinct increase at higher pressures.

The variation of the specific heat at constant pressure with the temperature is illustrated by the following table taken from Wiedemann :

Gas.	0°	100°	200°
Carbon dioxide -	0·1952	0·2169	0·2387
Ethylene - -	0·3364	0·4189	0·5015
Nitrous oxide - -	0·1983	0·2212	0·2442
Ammonia - -	0·5009	0·5317	0·5029

No variation of the specific heat of the simpler gases could be detected between $-80°$ and $200°$. Later experiments led Le Chatelier* to assume a temperature variation for gases also, and he proposed the formula $c_{p,\,w} = 6{\cdot}5 + aT$ for the true molecular heat $c_{p,\,w}$ of all gases. The value of a is larger the more complex the molecule. For the diatomic gases H_2, O_2, N_2, CO, a has the nearly constant value 0·001. Nernst† has shown that this equation is not satisfied at high temperatures, and proposes to substitute for it :

$$c_{p,\,w} = 3{\cdot}5 + n1.5 + aT,$$

where n is the number of atoms in the molecule.

Holborn and Henning‡ give the following formulae for the mean molecular heat between 0 and $t°$ C. :

For N_2, $c_{p,\,m,\,0-t°} = 6{\cdot}454 + 0{\cdot}0005t$,
,, CO_2, $c_{p,\,m,\,0-t°} = 8{\cdot}824 + 0{\cdot}00323t - 0{\cdot}00000079t^2$,
,, H_2O, $c_{p,\,m,\,100-t°} = 8{\cdot}423 - 0{\cdot}00030t - 0{\cdot}00000079t^2$.

The quantity of heat c_v which is necessary to raise the temperature of unit mass 1° C. at constant volume, is much more difficult to determine than the specific heat at constant pressure. Owing to the very low density of gases we should either have

* *Zeit. f. physical. Chemie*, **1**, 456 (1887).
† *Göttinger Nachrichten*, 1906, 1. ‡ Drudes, *Ann.* **23**, 809 (1907).

to take very small masses or very large volumes for a determination, and in both cases the sources of error would be considerable. Joly* tried to solve this problem with the aid of his steam calorimeter (p. 17), which he modified so as to enable him to use a differential method. Two hollow spheres of copper of 158 cubic centimetres capacity, and exactly equal water value, were suspended from either arm of a balance and placed in the steam chamber. One of the spheres was evacuated, and the other was filled with the gas under investigation. The specific heat of the gas can be calculated from the difference in weight of the water condensed on the two spheres. Experiments with air and carbon dioxide showed that the mean specific heat increases very slightly with the pressure between 12° and 100°. Joly gives the following values for $c_{v,\,m}$:

	1 atm.	26·6 atm.
Air - - -	0·17154	0·17225

Rudge,† in a recent determination with the water calorimeter, found for carbon dioxide at about 500 atmospheres pressure the extraordinarily high value $c_v = 0{\cdot}45$.

Mallard and Le Chatelier,‡ Langen§ and Pier ‖ make use of a different, and probably much more accurate, method for the determination of c_v. These investigators allow a mixture of gases to explode in a closed vessel, and determine the maximum pressure attained during the explosion. From the maximum pressure we can calculate the maximum temperature by the gas laws. Knowing the heat of reaction Q, evolved during the explosion, we can calculate the mean specific heat of the products of the reaction, or of an inert gas mixed with them, according to our fundamental equation : $Q = c_v(t_2 - t_1)$.

The most accurate determinations by this method, which is attended with considerable experimental difficulty, were made by Pier in Nernst's laboratory. The pressure produced by the explosion was measured by means of a flexible membrane with a mirror attached. The movement of a beam of light reflected

* *Proc. Roy. Soc.* **41**, 352 (1886).

† *Proc. Cambridge Phil. Soc.* **14**, 85 (1907). ‡ *Wied. Beibl.* **14**, 364 (1890).

§ Cf. Langen, *Mitteil. über Forschungsarbeiten*, Heft 8, Berlin, 1903.

‖ *Zeit. f. physical. Chemie*, **62**, 385 ; **66**, 6. *Zeit. f. Elektrochemie*, **15**, 536 (1909) ; **16**, 897 (1910).

from the mirror was recorded photographically.* On the assumption that the molecular heat of the monatomic gas, argon, is equal at all temperatures to 2·977, as the kinetic theory of gases demands,* Pier obtained the following values for the mean molecular heat at constant volume of the gases, hydrogen, nitrogen, oxygen, and water vapour, between 0° and 2300° :

H_2O,† $\quad c_{v,m} = 6{\cdot}065 + 0{\cdot}0005t + 0{\cdot}2 \times 10^{-9} \times t^3$,

$O_2 = N_2$, $\quad c_{v,m} = 4{\cdot}900 + 0{\cdot}00045t$,

H_2, $\quad c_{v,m} = 4{\cdot}700 + 0{\cdot}00045t$.

Nernst ‡ gives the following table for the true molecular heat c_v of a number of gases at varying temperatures :

Gas.	0°	100°	300°	500°	1200°	2000°
Ar - - - - -	2·98	2·98	2·98	2·98	2·98	2·98
H_2 - - - - -	4·75	4·78	5·02	5·20	5·8	6·5
$N_2 = O_2 = CO = HCl$ -	4·90	4·93	5·17	5·35	6·0	6·7
Cl_2 - - - - -	5·85	5·88	6·12	6·30	7·0	—
H_2O - - - - -	4·93	5·97	6·45	6·95	8·62	ca. 14
$CO_2 = SO_2$ - - -	6·80	7·43	8·53	9·43	11·2	ca. 14
NH_3 - - - - -	6·62	6·82	7·41	8·52	—	—
$(C_2H_5)_2O$ - - -	ca. 23	ca. 32·6	41·6	—	—	—

In general, the specific heat of gases rises with the temperature. The more complex the molecule, and the larger the value of the specific heat at 0°, the more rapid is the increase with the temperature. It has been found of late that the specific heat c_p of certain gases increases as the temperature is lowered to near the condensation point. Thus, Scheel and Heuse§ found for air :

	20°	−183°
c_p (per 1 g.)	0·2408	0·2525

Knoblauch and Mollier‖ obtained similar results for steam.

* Cf. Chap. IV.

† About 5 % too high, according to Bjerrum (*Zeit. f. Elektrochem.* **18**, 101, 1912).

‡ *Zeit. f. Elektrochem.* **17**, 272 (1911). § *Ann. d. Physik*, **37**, 79 (1911).

‖ *Zeit. des Vereins Deutscher Ingenieure*, **53**, 665 (1911).

CHAPTER III.

THE EQUIVALENCE OF HEAT AND WORK. THE FIRST LAW OF THERMODYNAMICS.

1. The first calculation of the mechanical equivalent of heat by J. R. Mayer.

The experiments described in the last paragraphs show that the specific heat c_p of gases at constant pressure is greater than the specific heat c_v at constant volume; or, in other words, more heat is necessary to raise the temperature of a gas 1° C. when the gas expands against a constant external pressure than is required if its volume is kept constant. J. R. Mayer, in 1842, was the first to recognise clearly that this greater absorption of heat is determined by the work done against the external pressure during expansion. The production of work is accompanied by an absorption of heat.

The reverse process, *i.e.* the production of heat when work is done, was discovered at the beginning of the nineteenth century. The exponents of the material theory of heat, guided by the assumption of the constancy of the heat substance in nature, explained the evolution of heat on turning metals by a supposed decrease in their specific heat. Count Rumford showed, however, by experiments on the large scale that the rise in temperature caused by the boring of a cannon cannot be accounted for by the decrease in the specific heat of the turnings. In 1798 he was the first to state clearly that the motion of the horses, which were used to drive the drill, was the true cause of the observed rise in temperature.

An experiment of Davy is equally important historically.

Davy observed that two pieces of ice could be made to melt by rubbing them against one another. The latent heat of fusion used up in this process could only have been produced by the work done against friction. Many other phenomena, such as the warming of the hands by rubbing them against one another, the production of fire by rubbing wood against wood, or steel against flint, etc., which had been familiar for hundreds of years, all pointed to the same conclusion. These facts were not, however, thought worthy of much attention by scientists until in the year 1842 Julius Robert Mayer, a physician of Würtemberg, enunciated the law of the equivalence of heat and work. This law states that the heat produced is proportional to the work done in its production; and conversely, when work is obtained from heat, the heat which disappears is in the same constant ratio to the work obtained. Thus, if an amount of work w is expended in boring a cannon, and a quantity of heat Q calories is liberated in the process, the quantity of work $n \,.\, w$ will be accompanied by the production of $n \,.\, Q$ calories. The constant ratio $\frac{w}{Q} = J$ is called the mechanical equivalent of heat. Its numerical value is independent of the manner in which the heat is produced by work. It is the same for the boring of metals; for the friction of solid or of liquid bodies against one another, etc. Conversely, if we convert heat into mechanical work, the ratio of the work done to the heat which has disappeared is again equal to J under all circumstances.

The inspiration to this fundamental discovery came to Mayer on a voyage in the Tropics. While in Java he had occasion to bleed some patients, and was struck by the intense red colour of the venous blood. It occurred to him that the reduced combustion in the body must correspond to the reduction in the radiation of heat to the surroundings. As the mechanical work done by a man in the Tropics is about the same as in a colder climate, it appeared to him that this constant amount of work required a constant amount of heat. Mayer generalised this qualitative result intuitively, and stated his conclusion explicitly in the form of the quantitative law which we have enunciated above, and showed, at the same time, what was then the only

possible way of calculating the numerical value of the mechanical equivalent J from known data.

Before discussing this calculation, it will be necessary to explain the term mechanical work and how it may be measured.

Mechanical work is defined as the product of a force, and the distance throughout which the force is active. The amount of work $P \cdot h$ is expended when a weight P is raised a height h, and conversely the same amount of work $P \cdot h$ is done by the weight P in falling from the height h. The same amount of work is necessary to raise 1 kg. 10 m. as is required to raise 10 kg. 1 m. The technical unit of force is the weight of 1 kg., the unit of length 1 m. In these units the unit of work is called 1 kilogrammeter (kgm.). In the absolute system of units the unit of force is the dyne, *i.e.* the force which produces an acceleration of 1 cm. per second per second in the unit of mass (the mass of 1 cubic cm. of water at 4° C. = 1 gr.). The unit of length is 1 cm., so that the unit of work 1 erg is equal to 1 dyne × 1 cm.* The relation between 1 kgm. and 1 erg may be deduced as follows. The force with which 1 kg. is attracted to the earth produces an acceleration of 981 cm.† per second per second in a mass of 1000 gr. This force is, therefore, equal to 981,000 dynes, so that

$$1 \text{ kgm.} = 98{,}100{,}000 \text{ ergs.}$$

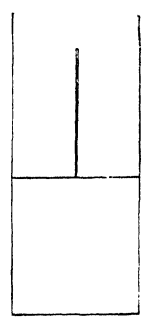


FIG. 13.

Mayer's calculation of the mechanical equivalent of heat is based on the difference between the specific heats c_p and c_v for air. Consider unit mass of air (1 g.) enclosed in a cylindrical vessel by means of a movable piston (Fig. 13). An amount of heat c_v will be required to raise the temperature of the gas 1° if the piston be prevented from moving. On the other hand, if the piston is free to move so that only the pressure of the atmosphere p is exerted on it, a greater amount of heat c_p will be required to raise the temperature of the gas 1°, and,

* Ostwald proposes the term one joule for the quantity of work 10^7 ergs, and one kilojoule for 1000 times this quantity, *i.e.* 10^{10} ergs. These terms do not, however, seem to have come into general use.

† Acceleration due to gravity in central Germany.

at the same time, the expansion of the gas will cause the piston to be pushed back a distance ds against the pressure p. According to Mayer, the difference between these two amounts of heat $c_p - c_v$ is proportional to the work done w, so that

$$w = J(c_p - c_v).$$

The force acting on the piston during the displacement ds is equal to the product of the pressure p and the cross-section o of the piston, since pressure is defined as the force acting on unit of surface. Hence

$$w = p \,.\, o\, ds = p \,.\, dv,$$

if we write dv for the increase in the volume of the gas on raising the temperature 1°. This increase in volume is, by Gay-Lussac's law, the 273rd part of the volume which unit mass of air occupies at 0°. Hence

$$dv = \tfrac{7}{2}\tfrac{7}{7}\tfrac{0}{3} = 2{\cdot}8 \text{ c.c. (for } p = 1 \text{ atm.)}.$$

The force exerted by a pressure of 1 atm. on a piston 1 sq. cm. in area is equal to the weight of a column of mercury 76 cm. in cross section. Hence $p = 76 \times 13{\cdot}6 = 1033$ g. $= 1{\cdot}033$ kg., so that

$$w = \frac{1{\cdot}033 \times 2{\cdot}8}{100} = 0{\cdot}029 \text{ kgm.}$$

According to the data which were available to Mayer at that time, the specific heats of air were $c_p = 0{\cdot}267$ and $c_v = 0{\cdot}1875$, so that

$$J = \frac{0{\cdot}029}{0{\cdot}079} = 0{\cdot}367.$$

The quantity of heat required to raise 1 g. of water 1°, converted into work, would be capable of raising a weight of 0·367 kg. by 1 m. According to later measurements, $c_p - c_v = 0{\cdot}068$ and $w = 0{\cdot}0294$, so that

$$J = \frac{0{\cdot}0294}{0{\cdot}068} = 0{\cdot}433 \text{ kgm.}$$

The technical unit of heat is the great calorie, *i.e.* the quantity of heat which is necessary to raise the temperature of 1 kg. of water 1°. This amount of heat is capable of doing 367 or rather 433 kgm. of work.

Mayer's calculation cannot be looked upon as a proof of the law of the equivalence of heat and work. It is merely a deduction

from it. The validity of the law can be demonstrated in two ways. First, by showing experimentally that the mechanical equivalent of heat is independent of the manner in which work is converted into heat and *vice versa*; or, secondly, by proving that the law is a necessary consequence of some generally recognised experience. These two methods were employed independently and nearly simultaneously, the first by Joule, and the second by Helmholtz.

2. The experimental confirmation of the equivalence of heat and work.

James Prescott Joule recognised the great importance and the general applicability of the law of equivalence at about the same time as Mayer, and proved the law by a number of very careful and ingenious experiments. He converted work into heat in the most diverse ways, and measured the work done and the heat produced. The more important of his experiments will be discussed in the following:

1. Air is compressed to 22 atm. in a vessel which is kept in a water calorimeter. The work done during compression can be calculated from the initial and final pressures and volumes. The work done is completely converted into heat which is communicated to the calorimeter. The mean of several determinations by this method gave for one great calorie $J = 436{\cdot}1$ kgm. The same experiment carried out in the reverse direction is an example of the conversion of heat into work. When the compressed gas is allowed to expand, heat is abstracted from the calorimeter and its temperature is lowered. Three experiments of this sort gave for J the values 449·8, 446·5, and 416·8 kgm.

2. In another of Joule's experiments, paddle wheels in a liquid were driven by means of a weight and pulley, and the work done against friction was calculated from the height through which the weight had fallen. Rotating the paddles in water, Joule found $J = 424{\cdot}30$. For friction in mercury the mean of one series of measurements gave 424·37, and that of a second series 425·77 kgm.

3. Two cast-iron wheels were made to rotate and rub against one another under mercury, which served as the calorimeter

fluid. Joule obtained by this method the values 426·14 and 425·00 kgm.

4. By forcing water through narrow openings or capillaries, work is also converted by friction into heat. Joule forced water through small holes in a cylinder by means of a piston, and obtained by this method $J = 424{\cdot}6$ kgm.

5. A coil of wire wound round an iron core was made to rotate in a calorimeter between the poles of a horse-shoe magnet. Electric currents are produced in the wire, and are in turn converted into heat owing to the electrical resistance of the coil. The conversion of work into heat takes place indirectly by means of the electric current. By this method Joule obtained the mean value $J = 459{\cdot}62$ kgm. for the mechanical equivalent of heat.

6. Experiments of a similar nature were performed somewhat later by Hirn, who determined the quantity of heat produced by a blow. A small hollow vessel of lead filled with water and furnished with a thermometer was placed between an iron ram and a suspended block of stone. When the block of stone is struck by the ram, it is displaced to a less extent than corresponds to the intensity of the blow, while, at the same time, the temperature of the lead vessel and its contents is raised. Hirn calculated the mechanical equivalent of heat from the difference between the work done by the blow and that done in displacing the block, and found $J = 425{\cdot}2$ kgm.

7. Hirn did another very important experiment to determine the amount of work obtained from heat. He determined the work done by a steam engine, and equated it to the difference between the heat supplied to the boiler and the heat given up to the condenser. From the mean of Hirn's determinations Clausius calculated the value $J = 413$ kgm.

These experiments show no more than that the mechanical equivalent of heat, determined in various ways by converting work into heat or *vice versa*, is roughly constant. There are considerable differences in the values found by the various methods, so that these experiments cannot be regarded as proving the law of the exact equivalence of heat and work. It might still be possible that the amount of work done in producing the unit of heat should vary slightly with the method by which

the heat is produced. It was, therefore, found to be necessary to increase the accuracy of the determinations as much as possible, and to ascertain whether the deviations were due to errors of experiment or whether they had a real significance.

Of late years a number of very careful measurements of the mechanical equivalent of heat have been undertaken for this purpose. The methods employed in these measurements are the same in principle as those of Joule, and differ only in the greater refinement of the apparatus. The methods which have been employed hitherto are all based on the production of heat by friction or by the electric current. The results are tabulated below. In column 3 is given the number of ergs which is equivalent to a small 15° calorie.

Name of the Investigator.	Method.	J
Rowland - - - -	Friction in water	$4{\cdot}187 \times 10^7$
Miculescu - - - -	Friction in water	$4{\cdot}183 \times 10^7$
Griffiths - - - -	Production of heat by the electric current	$4{\cdot}192 \times 10^7$
Schuster and Gannon - -	,,	$4{\cdot}191 \times 10^7$
Callendar-Barnes - - -	,,	$4{\cdot}187 \times 10^7$

Scheel and Luther* considered $J = 4{\cdot}188 \times 10^7$ ergs to be the most probable value. If we wish to translate this value into kilogrammeters and great calories, we must take the geographical position into consideration, since the acceleration of gravity varies with the latitude. At Berlin $g = 981{\cdot}23$, so that

$$J = \frac{4{\cdot}188 \times 10^7}{981{\cdot}23 \times 100} = 426{\cdot}8 \frac{\text{kgm.}}{\text{Cal.}}.$$

3. Helmholtz's proof. The law of the conservation of energy.

In 1847 Helmholtz published a paper entitled "Über die Erhaltung der Kraft"† (On the Conservation of Force). For centuries men have tried in vain to obtain perpetual motion, that is, to invent a machine which would produce useful work in perpetuity without any expenditure of trouble or money.

* *Zeit. f. Elektrochemie*, **14**, 743 (1908).

† Ostwald, *Klassiker der exakten Wissenschaften*, Nr. 1.

The impossibility of perpetual motion was so well recognised in the scientific world that the Paris Academy of Science, as early as the eighteenth century, determined to refuse to give any more consideration to reputed solutions of this problem than they would to attempts at the quadrature of the circle. Helmholtz recognised the connection between this experiment and the mutual convertibility of heat and work. If the mechanical equivalent of heat were not always the same, so that we might obtain from a given amount of work by friction more heat than would be necessary to produce this amount of work in a steam engine, we should be able by combining these two processes to construct a machine which would produce heat constantly from nothing, because the sum of the work expended and produced in the machine would be equal to nothing. The heat obtained in this way could be converted again into work, and the dream of the medieval philosophers, of obtaining work from nothing, would be fulfilled. The impossibility of perpetual motion compels us to conclude that when heat is obtained from work, or *vice versa*, the quantities of work and heat which appear and disappear must always be exactly proportional to one another, or, in other words, heat and work are equivalent.

Helmholtz, using the nomenclature of his time, designated that which can produce mechanical work as "force." Heat must, therefore, also be looked upon as a force, and likewise all things which can be converted into work or heat directly, such as electricity and light. As work cannot be created from nothing, it follows that the sum of the "forces" remains constant in all natural processes.

To avoid confusion with the usual conception of force in dynamics (force = mass × acceleration), this unchangeable power of doing work was termed "energy."* We may now sum up

* The word "energy" was used by Thomas Young in 1807. The best of the numerous definitions for this conception is probably that proposed by William Thomson (Lord Kelvin) in 1851, and accepted by M. Planck. It is as follows: The energy (power of doing work) of a material system is the sum measured in mechanical units of work, of all the effects which are produced outside the system, when the system is made to pass in any manner from the state in which it happens to be to a certain arbitrarily fixed initial state. (See also Planck, *Das Prinzip der Erhaltung der Energie*, Leipzig, 1887, 2nd edition, 1910.) In this treatise Planck gives an excellent exposition of the law of the conservation of energy and of its historical developments.

the results of our conviction of the impossibility of perpetual motion in the following sentence. In all processes which take place in an isolated system, the energy of the system remains constant. The law of the conservation of energy, also called the first law of thermodynamics, or more shortly "the first law," is the most universal natural law that we know. As heat or work may be produced by means of electric currents or radiant light (Röntgen rays, etc.), and also by chemical reactions, we speak of thermal energy, mechanical energy, electrical, radiant, and chemical energy. These various forms of energy can all be transformed into one another in definite proportions, but heat energy occupies a unique position. It is always possible to convert definite amounts of any of the other forms of energy into the equivalent amount of heat, but the transformation of heat into other forms of energy is restricted by circumstances in a definite way (see Chapter V.).

The wish to attain to a uniform conception of nature made it desirable to express the various natural qualities (motion, heat, light, etc.) in a quantitative manner. The law of the conservation of energy was a very great step in this direction. If it be possible to transform these various qualities into one another in definite quantitative proportions, they cannot be intrinsically distinct from one another, but must be looked upon as different forms of one and the same original cause. At first there appeared to be little doubt that the common cause of the various forms of energy was motion. The thermal, electrical, and radiant states of a body are supposed to be determined by peculiar forms of motion in its ultimate particles. The absorption of heat, electricity, or light increases, while their emission diminishes the kinetic or potential energy of the ultimate particles. Recent researches have shown that a perfectly evacuated space may possess energy when under the influence of the electromagnetic field, or when traversed by heat or light radiation. We must, therefore, either discard or extend the old mechanical theory. Attempts have been made to extend the theory on the basis of electro-dynamical conceptions, but we cannot discuss them here. According to the first law, the energy of a body or of a system of bodies at any instant of time depends only on its

state, that is to say, on its temperature, its volume, its pressure, its state of electrification, etc., and is independent of the path or process by which the body has arrived at this state. It is only under these conditions that the change in energy between state (i) and state (ii) is solely determined by the initial and final states of the body, and not by the way in which the change of state has been produced. If this were not the case and there were a path between (i) and (ii) by which the system could absorb more energy than by another path, we could allow the system to return from (ii) to (i) by this second path, so that the system would return to state (i) with more energy than it had before. By perpetual repetition of this process we could create unlimited amounts of energy in an isolated system, and by using this energy to do work we could construct a perpetual motion machine.

The energy U of a body is, therefore, a single-valued function of its variables of condition (pressure, temperature, volume, etc.), so that $U=f(p, t, v \ldots)+U_0$. The volume of a gas, for example, is a single-valued function of its pressure and temperature. U_0 is an additive constant which cannot be determined by thermodynamics, and measures the energy of an arbitrarily chosen initial condition of the body. If we increase the variables of condition by the amounts dp, dT, dv, etc., the energy is changed by the amount dU, which is called the total differential of the single-valued function U. By the rules of the differential calculus the total differential dU of a function U of the variables $x, y, z \ldots$ is given by the equation

$$dU=\frac{\partial U}{\partial x}dx+\frac{\partial U}{\partial y}dy+\frac{\partial U}{\partial z}dz+\ldots.$$

$\frac{\partial U}{\partial x}, \frac{\partial U}{\partial y} \ldots$ are the partial differential coefficients of the function U with respect to x, y, z.

Excluding electrical and magnetic processes, the state of a body is determined by its volume, its temperature, and its pressure. These three quantities are not independent of one another, but are connected, as we know, by an equation of condition (*e.g.* $pv=RT$ for gases) which determines the value

of the third variable when the other two variables are given. The energy of a body subject only to thermal changes and to compression or dilatation is, therefore, determined completely when two of its variables of condition are given. It is a matter of indifference theoretically whether we choose p and T, or p and v, or v and T as independent variables. In practice we should make our choice so that the experimental determinations of the variables may be as simple as possible. In what follows we shall restrict ourselves in the first instance to thermal changes and to changes of volume, and shall take the temperature T and the volume v as independent variables. The general equation for the energy of the body is then

$$U = f(v, t) + U_0.$$

If we make the body absorb an amount dQ of heat its energy increases by the amount dU, and an amount dw of work will be done in consequence of expansion against the external pressure. By the law of the conservation of energy these quantities are connected by the fundamental equation

$$dQ = dU + dw. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

In the following we shall discuss some important applications of this equation.

CHAPTER IV.

APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS.

1. The kinetic theory of gases.

The kinetic theory of gases was first propounded by Daniel Bernoulli in 1738. It was rediscovered and worked out in detail about the middle of the nineteenth century by Krönig, Waterston, Maxwell, and above all by Clausius. According to the kinetic theory the molecules of a gas move in straight lines unless they are deflected from their path by impacts with other molecules or with the walls of the containing vessel. They, therefore, exert on every solid wall a pressure which is measured by the momentum which the molecules impart to the wall in unit time. As this momentum is proportional to the number of collisions per unit of time, and also to the momentum of each colliding molecule, we conclude that the pressure p of a gas in any closed vessel is proportional to the square of the velocity of its molecules. It is assumed in this that all the molecules have the same velocity. When this is not the case, the pressure can be shown to be proportional to the mean square of the velocity. In any case we may write

$$p = Kc^2.$$

Assuming that all the molecules have the same velocity, it is easy to calculate the value of K. Let n be the number of molecules contained in a cube of edge 1 cm. in length, and let m be the mass of each molecule. Every molecule which strikes the wall perpendicularly imparts to it the momentum $2mc$, since its velocity is changed from $+c$ to $-c$. In order to obtain

the pressure, *i.e.* the total momentum imparted to the wall in unit time, we must multiply the quantity $2mc$ by the number of perpendicular impacts which take place in 1 second on 1 cm². of the wall. We may calculate this number as follows. Suppose the molecules, which ordinarily would have velocities in all directions of space, to be resolved into three groups of molecules moving in three perpendicular directions. The number of molecules which strike the wall perpendicularly is then $\frac{1}{3}n$. Each molecule moves 2 cm. between two consecutive impacts with the same wall. Since the velocity of the molecule is c, the time between two impacts will be $\frac{2}{c}$ seconds. The number of impacts per second on each cm². of the wall is, therefore, $\frac{1}{3}n \cdot \frac{c}{2} = mc/6$, and hence the pressure

$$p = nc/6 \cdot 2mc = nmc^2/3.$$

Let N be the number of molecules in 1 mol., *i.e.* in the gramme-molecular weight, and v the volume occupied by these N molecules. We have then

$$n = \frac{N}{v} \quad \text{and} \quad pv = Nmc^2/3.$$

If we assume that the velocity c of the molecules depends only on the temperature of the gas, we are led directly to Boyle's law, $pv = \text{constant}$ (for constant temperature).

If we assume further that the total energy U of the gas is entirely kinetic energy of the rectilinear motion of the molecules, we obtain

$$U = \frac{Nmc}{2} = \tfrac{3}{2}pv.$$

The energy of the gas is then a function of the temperature alone $U = f(T)$. From this it follows that

$$\frac{\partial U}{\partial v} = 0, \quad \text{since} \quad dU = \frac{\partial U}{\partial T}dT + \frac{\partial U}{\partial v}dv.$$

The form of the function $U = f(T)$ cannot be deduced from the assumptions we have made hitherto. The fact that bodies communicate no heat energy to one another when they have the same temperature (page 1), in the light of the laws of impact,

tells us only that the temperature must be a single-valued function of the square of the velocity c^2. The form of this function must depend on the scale in which we measure the temperature. From the empirical law of Charles we obtain (for ideal gases) $pv = RT$, and hence $U = \frac{3}{2}RT$. The energy of a gas is, therefore, proportional to the absolute temperature. Measuring the temperature on the centigrade scale, we have $pv = R(273+t)$, so that

$$U = \tfrac{3}{2}R(273+t).$$

For perfect gases we may now write the fundamental equation (1), p. 83, in the following form :

$$dQ = \frac{\partial U}{\partial T}dT + dw. \quad \ldots\ldots\ldots\ldots\ldots\ldots (1a)$$

The physical meaning of the temperature coefficient $\frac{\partial U}{\partial T}$ becomes apparent from the following consideration. $\frac{\partial U}{\partial T}$ is the amount of heat which the gas absorbs when its temperature is raised 1° without doing work. No work is done when the gas is heated at constant volume, so that

$$\frac{\partial U}{\partial T} = c_v.$$

The specific heat of a perfect gas at constant volume should, therefore, be independent of the temperature and equal to $\frac{3}{2}R$.

From what was said on page 76 it follows that the work done by a gas when its volume is increased by dv, is $dw = p\,dv$. Equation (1) may, therefore, be written for perfect gases in the form

$$dQ = c_v\,dT + p\,dv. \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Some important deductions can be made from equation (2).

2. Application to perfect gases.

The oldest and most important experimental proof of the correctness of equation (2) was given by Gay-Lussac. If we allow a gas to expand without absorption or loss of heat, and so that no external pressure has to be overcome in the expansion, then dQ and $p\,dv$ are both zero. From equation (2) it follows that $dT = 0$ also, *i.e.* there should be no change in temperature. In accordance with this Gay-Lussac found that when a gas

was allowed to expand into a vacuum its temperature was not altered. This result is, however, only approximately correct, since the gases which we find in nature are not perfect gases. Joule and W. Thomson found later by more careful measurements that it is possible to observe a slight change in temperature when a gas expands without doing work. For all gases, with the exception of hydrogen, there is a fall in temperature, for hydrogen there is a slight rise in temperature. We shall return to this so-called Joule-Thomson effect later on.*

Isothermal processes. If we conduct the compression or expansion of a gas so that its temperature remains constant, the change in volume is said to take place isothermally. This condition can be realised experimentally by keeping the gas during expansion in a thermostat of large capacity for heat, and by causing the change in volume to take place so slowly that the gas always maintains the constant temperature of its surroundings. In this case we have $dT=0$ and $dQ=p\,dv$. The heat absorbed by the gas is completely converted into work.

The equation $dQ=p\,dv$ assumes the form

$$Q=\int_{v_1}^{v_2} p\,dv$$

for a finite change in volume from v_1 to v_2.

The integration can only be carried out when p is known as a function of v in the whole interval from v_1 to v_2, *i.e.* when we know the pressure which has to be overcome during expansion for every value of v between v_1 and v_2.

We shall assume that this pressure is equal throughout to the pressure in the interior of the gas. We have then

$$p=\frac{RT}{v},\quad \text{and hence}\quad Q=\int_{v_1}^{v_2}\frac{RT\,dv}{v}=RT\log_e\frac{v_2}{v_1}. \quad \ldots\ldots(3)$$

* In most text-books equation (2) is deduced as follows: By the first law we have $dQ=dU+dA=\frac{\partial U}{\partial T}dT+\frac{\partial U}{\partial v}dv+p\,dv$. Gay-Lussac's experiment shows that the energy of a gas is independent of its volume, so that $\frac{\partial U}{\partial v}=0$. Hence $dQ=c_v dT+p\,dv$. This is the older demonstration historically, but it makes use of an empirical fact, which at first sight has no apparent connection with our other knowledge of the behaviour of gases. For this reason it appeared to me that the above demonstration, which is a deduction from the kinetic theory of gases, and is confirmed by Gay-Lussac's experiment, was preferable from the didactic point of view.

This is an expression for the maximum amount of work which can be done in the expansion of a gas from volume v_1 to volume v_2 at constant temperature, for the greatest pressure against which expansion can take place is that which is equal to the internal pressure of the gas. If the external pressure is smaller than the internal pressure, the work done will also be smaller than in the limiting case, in which both are equal. On the other hand, when a gas is compressed, the work done in the compression is a minimum when the external and internal pressures are equal to one another. In the limiting case, which is characterised by the condition

$$p = \frac{RT}{v},$$

the work done in the expansion from v_1 to v_2 is equal to the work which would be required for the compression from v_2 to v_1. The change in volume can then be reversed without changing the store of work or heat, *i.e.* the energy content, of the surroundings. A process of this sort which can be reversed completely without absorption of energy from the outside is called a *reversible* process.

For the reversible change in volume of an ideal gas, we have the equation

$$Q = RT \log \frac{v_2}{v_1}.$$

According to Boyle's law, the product of pressure and volume is constant at constant temperature, so that

$$p_2 v_2 = p_1 v_1, \quad \text{or} \quad \frac{v_2}{v_1} = \frac{p_1}{p_2}.$$

Hence

$$Q = RT \log \frac{p_1}{p_2}. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3a)$$

The heat absorbed or given out, or the equivalent amount of work done or expended is, therefore, dependent only on the ratio of the initial and final volumes, and not on their absolute values. The same amount of work is done in compressing a gas from 1 to 2 atm. as is necessary to compress the same amount of gas from 100 to 200 atm.

The following example will explain the use of the equations

(3) and (3*a*) in calculations. We shall calculate the amount of heat which is produced when 1 litre of a gas at 25° C. is compressed from 1 to 2 atm. The work done in compressing 1 mol. of the gas is

$$w = -RT \log \frac{p_1}{p_2}.$$

If 1 litre contains n mols., the work done is

$$-nRT \log \frac{p_1}{p_2} = nRT \log 2, \text{ if } p_1 = 1 \text{ and } p_2 = 2.$$

The volume of 1 mol. at 0° and a pressure of 1 atm. is 22·4 l. (by page 61). At T° the volume is, therefore, $\frac{22{\cdot}4T}{273}$, so that at 25° C. the volume will be 24·4 l. There are, therefore, $n = \frac{1}{24{\cdot}4}$ mols. in 1 litre at 25° C. and a pressure of 1 atm. The numerical value of the gas constant R depends on the system of units in which we wish to express the work done. In the absolute system (based on the units gram, centimetre, and second) we may calculate R as follows: A pressure of 1 atm. exerts a force on 1 sq. cm. equal to the weight of a column of mercury 76 cm. high, and 1 sq. cm. in cross section. Hence $p = 76 \times 13{\cdot}6 \times 981$.* Since 1 mol. at 0° and this pressure occupies the volume 22·4 l. = 22400 c.c., we have

$$R = \frac{pv}{T} = \frac{76 \times 13{\cdot}6 \times 981 \times 22400}{273} = 8{\cdot}3 \times 10^7 \text{ ergs.}\dagger$$

Hence the amount of work necessary to compress the litre of gas from 1 to 2 atm. at 25° C. is

$$\begin{aligned} w &= -nRT \log \frac{p_1}{p_2} = \frac{8{\cdot}3 \times 10^7 \times (273+25)}{24{\cdot}4} \log 2 \\ &= \frac{8{\cdot}3 \times 10^7 \times 298 \times 2{\cdot}3 \times 0{\cdot}301}{24{\cdot}4}\ddagger \\ &= 7{\cdot}0 \times 10^8 \text{ ergs.} \end{aligned}$$

* 13·6 is the specific gravity of mercury, and 981 is the acceleration due to gravity. Cf. pages 75 and 76.

† More exactly $8{\cdot}316 \times 10^7$ ergs.

‡ 2·3 is the factor by which the decadic logarithm must be multiplied in order to obtain the natural logarithm

To obtain the quantity of heat in calories which is equivalent to this amount of work, we must divide by the mechanical equivalent of heat $J = 4{\cdot}19 \times 10^7$. Hence

$$Q = \frac{7{\cdot}0 \times 10^8}{4{\cdot}19 \times 10^7} = 16{\cdot}7 \text{ cal.}$$

Change of temperature at constant pressure. Differentiating the equation $pv = RT$ on the assumption that the pressure p remains constant while the temperature is changed by dT, we obtain

$$p\,dv = R\,dT.$$

Combining this with (2), we obtain

$$dQ = c_v\,dT + R\,dT,$$

or

$$\frac{dQ}{dT} = c_v + R.$$

$\frac{dQ}{dT}$ is the specific heat of the gas at constant pressure. Hence

$$\frac{dQ}{dT} = c_p = c_v + R,$$

or

$$c_p - c_v = R.$$

The quantities c_p and c_v here refer to the gram-molecular weight of the gas. The difference of the molecular heats of all gases is, therefore, constant and equal to R. By page 89 we have

$$R = 8{\cdot}3 \times 10^7 \text{ ergs} = \frac{8{\cdot}316 \times 10^7}{4{\cdot}19 \times 10^7} \text{ cal.} = 1{\cdot}985 \text{ cal. per } ^\circ \text{C.}$$

The molecular heat at constant pressure is, therefore, roughly 2 cal. greater than the molecular heat at constant volume for all gases which approach in their behaviour to the ideal gas.

Comparing the tables on pages 69 and 72 we obtain an approximate confirmation of this consequence of the theory.

Gas.	C_p*	C_v*	$C_p - C_v$
H_2 - -	6·82	4·70	2·1
N_2 - -	6·83	4·90	1·93

* At room temperature.

Adiabatic processes. Ratio of the specific heats. If the gas is contained in a vessel, the walls of which are impermeable to heat or "adiabatic"* so that no interchange of heat with the surroundings is possible, the energy of the gas diminishes by the amount of the work done against the external pressure. On the other hand, if the gas is compressed, its energy increases by the amount of the work done in the compression. In the first case there is a fall, in the second a rise in the temperature of the gas. The magnitude of the change in temperature may be calculated from equation (2) as follows :

An adiabatic process is characterised by the condition

$$dQ = 0.$$

Hence $$-dU = -c_v\,dT = p\,dv.$$

If the change in volume is carried out reversibly, so that the external and internal pressures are equal to one another at every instant, we have

$$p = \frac{RT}{v}.$$

Hence $$-c_v dT = \frac{RT}{v}\,dv,$$

and $$-\frac{dT}{T} = \frac{R}{c_v}\cdot\frac{dv}{v} = \frac{c_p - c_v}{c_v}\cdot\frac{dv}{v}.$$

Writing the ratio of the specific heats for shortness $\frac{c_p}{c_v} = k$, and integrating between the limits v_1 and v_2 and T_1 and T_2, we have

$$-\log\frac{T_2}{T_1} = (k-1)\log\frac{v_2}{v_1},$$

or $$T_1 v_1^{k-1} = T_2 v_2^{k-1}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Hence, if 1 mol. of a gas is brought by compression or dilatation from volume v_1 to volume v_2, the final temperature T_2 and the final volume v_2 are connected with the initial temperature and volume T_1 and v_1 by equation (4).

The pressure p_2 at the end of this adiabatic change in volume is $p_2 = \frac{RT_2}{v_2}$. We have likewise $p_1 = \frac{RT_1}{v_1}$, and eliminating the

* From ἀδιαβαίνω.

temperatures between these equations and equation (4), we obtain equation (4*a*):

$$p_1 v_1^{\,k} = p_2 v_2^{\,k}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4a)$$

Finally, we may calculate the relation between the temperature and pressure in an adiabatic process. We have

$$v_1 = \frac{RT_1}{p_1}, \quad \text{and} \quad v_2 = \frac{RT_2}{p_2},$$

so that

$$p_1^{\,1-k} T_1^{\,k} = p_2^{\,1-k} T_2^{\,k}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4b)$$

For gases which conform to the conditions (p. 85) assumed in the kinetic theory of gases, we may calculate the value of k directly. For these gases

$$U = \tfrac{3}{2} RT,$$

and

$$c_v = \frac{\partial U}{\partial T} = \tfrac{3}{2} R.$$

Hence

$$\frac{R}{c_v} = \frac{c_p - c_v}{c_v} = k - 1 = \tfrac{2}{3}, \quad \text{so that} \quad k = \tfrac{5}{3}.$$

Before comparing this strikingly simple result of theory with the experimental observations, we shall discuss briefly the direct experimental methods by which k has been determined.

(*a*) *The method of Clement and Desormes.* A gas in the state v_0, p_0, T_0 is compressed or allowed to expand so quickly that during and immediately after the change of state the interchange of heat with the surroundings may be neglected. Under these conditions the change of state takes place adiabatically, and the variables v, p, and T which characterise the new state are connected with the initial variables v_0, p_0, T_0 by equation (4). If the gas expands $v > v_0$, $p < p_0$, and $T < T_0$. Sufficient time is then allowed to elapse to let the gas assume its initial temperature, which is also the temperature of the surroundings. The pressure will change during this process, and will ultimately assume the value p_1. If $T < T_0$, then $p_1 > p$.

For the first adiabatic change of state, we have

$$p_0 v_0^{\,k} = p v^k.$$

Further, since the temperature at the beginning and at the end of the experiment is T_0,

$$p_0 v_0 = p_1 v.$$

Hence $$\frac{v^k}{v_0^k}=\frac{p_0}{p}=\left(\frac{p_0}{p_1}\right)^k,$$

and $$k=\frac{\log\frac{p_0}{p}}{\log\frac{p_0}{p_1}}.$$

If the change in volume $v-v_0$, and hence also the change in pressure p_0-p and p_0-p_1 are small, we may write as a first approximation

$$\log\frac{p_0}{p}=\frac{p_0-p}{p_0} \quad \text{and} \quad \log\frac{p_0}{p_1}=\frac{p_0-p_1}{p_0}.$$

We have then $$k=\frac{p_0-p}{p_0-p_1}.$$

(*b*) Lummer and Pringsheim determined directly the change in temperature T_0-T consequent on an adiabatic change in volume. Air at a pressure p_0 a little greater than 1 atm. is contained in a large copper vessel 90 l. in capacity, which is kept in a water bath at the constant initial temperature T_0. On opening a stop cock air rushes out of the vessel until the pressure inside is equal to that of the external atmosphere, and the temperature falls simultaneously to T according to the equation $$p_0^{1-k}T_0^k=p^{1-k}T^k.$$

From this we derive $$k=\frac{\log\frac{p_0}{p}}{\log\frac{p_0}{p}+\log\frac{T}{T_0}},$$

and for $p=1$, $$k=\frac{\log p_0}{\log p_0+\log T-\log T_0}.$$

The temperatures T_0 and T were determined with great exactness by means of a bolometer in the interior of the vessel.*

(*c*) *The determination of k from the velocity of sound.* In the propagation of longitudinal waves (sound waves) in a gas, compressions and dilatations of the gas follow one another very rapidly. These compressions and dilatations may be regarded as taking place adiabatically, as the rate at which they follow

* Höhne (*Dissert.* Breslau, 1913) describes a method of carrying out this determination with 1 l. of gas.

one another is so rapid that the slow interchange of heat by conduction may be neglected. The velocity of sound is, therefore, dependent on the ratio of the specific heats k. Laplace deduced the following formula for the velocity of sound:

$$C = \sqrt{\frac{p}{d}k}.$$

p is the pressure and d the density of the gas. The velocity of sound C is connected with the wave-length λ and the frequency n by the equation $C = n\lambda$. We can, therefore, calculate C from a determination of the frequency for a known wave-length, or with the aid of dust figures by determining the wave-length of stationary waves for a known frequency. The first of these methods was used by Dulong, the second by Kundt, and many others after him, who determined the value of k for a large number of gases by this simple and accurate method.

The following table is a summary of the determinations of k which have hitherto been made for various gases and vapours:

Gas.	k	Gas.	k
Helium	1·67	Chlorine	1·32
Argon	1·67	Bromine	1·29
Mercury	1·67	Nitrous oxide	1·27
Air	1·40	Sulphur dioxide	1·26
Oxygen	1·40	Hydrogen sulphide	1·33
Nitrogen	1·40	Methan	1·32
Hydrogen	1·40	Ethylen	1·24
Carbonic oxide	1·40	Carbon disulphide	1·20
Nitric oxide	1·39	Chloroform	1·15
Hydrogen chloride	1·40	Ethyl alcohol	1·13
Hydrogen iodide	1·40	Benzene	1·11
Water vapour	1·33	Ethyl ether	1·06
Carbon dioxide	1·30		

The table shows that the theoretical deduction $k = \frac{5}{3}$ (p. 92) is only realised for the monatomic permanent gases, and also for mercury vapour, which is likewise monatomic. This also holds for certain metallic vapours not cited in the table. For all other gases $k < \frac{5}{3}$ and the difference $\frac{5}{3} - k$ is greater the more complicated the molecule and the more the gas in question deviates from the simple gas laws. Yet even where the laws of Boyle and Charles are followed with great exactness, as for

hydrogen, oxygen, and nitrogen, k is only equal to 1·4. We must, therefore, conclude that the assumptions made in the deduction of the equation $k=\frac{5}{3}$ do not hold for polyatomic gases.

These assumptions were: (1) The validity of Charles' law. (2) That the energy of the gas U consists entirely of the kinetic energy L of the rectilinear motion of the molecules. As diatomic gases obey Charles' law, we conclude that the second assumption must be at fault. The equation $U=L$ does not hold for polyatomic gases, and we must substitute for it the equation $U=L+P$.

This result can be accounted for without difficulty by the kinetic theory. P is the internal energy of the molecules. If the molecule consists of a single atom $P=0$, if the molecule consists of several atoms, P is determined by the motion of these atoms inside the molecule. These internal motions may consist of rotations about one or more axes, or of oscillations about centres of equilibrium. Gay-Lussac's experiment shows that the energy of a gas is independent of its volume and depends only on its temperature, so that

$$\frac{\partial U}{\partial v}=0 \quad \text{and} \quad U=L+P=c_v T.$$

Hence L and P must both be proportional to the temperature, and hence also to one another. When, therefore, the temperature of a gas which obeys the simple gas laws is raised, the kinetic energy of the molecules increases in the same ratio as their internal energy, so that we have

$$P=h\,.\,L=h\,.\,\tfrac{3}{2}RT.$$

We can calculate the ratio $\frac{P}{L}=h$, however, from the empirical value of k, and can therefore tell how much of the total energy of the gas is due to the kinetic energy L, and how much to the internal energy of the molecules P. From the equations

$$U=c_v T=L+P=L(1+h)=\tfrac{3}{2}R(1+h)T,$$

we have
$$1+h=\frac{2c_v}{3R}=\frac{2c_v}{3(c_p-c_v)}=\frac{2}{3(k-1)},$$

and
$$h=\frac{2}{3(k-1)}-1=\frac{5-3k}{3(k-1)}.$$

For diatomic permanent gases $k=1{\cdot}4$. Hence

$$h=\frac{0{\cdot}8}{1{\cdot}2}=\frac{2}{3},$$

for water vapour $k=1{\cdot}33$, so that

$$h=\tfrac{1}{1}=1.$$

For benzene $k=1{\cdot}11$. Hence

$$h=\frac{1{\cdot}67}{0{\cdot}33}=5,$$

for ether vapour $k=1{\cdot}06$, and

$$h=\frac{1{\cdot}82}{0{\cdot}18}=10.$$

The intramolecular energy is more predominant the more complicated the molecule. If $\frac{P}{L}=H=\infty$, we have $k=1$, and the specific heat at constant pressure and at constant volume differ by an infinitely small quantity. Solid and liquid bodies approximate to this limiting case.

With the exception of monatomic gases, c_p and c_v are independent of the temperature only for a very limited range of temperature and pressure. We should, therefore, expect the ratio of the specific heats k to vary with the temperature and pressure also. According to the experiments on air of P. P. Koch,* k increases very considerably with the pressure, and this increase is greater the lower the temperature.

Thus - -	$p=25$	100	200 atm.
At 0° - -	$k=1{\cdot}473$	1·646	1·828
„ −79° -	$k=1{\cdot}405$	2·001	2·413

The increase of k depends on the deviations from the simple gas laws. According to Van der Waals' theory, k must be a maximum when the product pv is a minimum. This relationship is confirmed qualitatively by Koch's experiments.

3. Real gases.

For real gases the simple gas laws no longer hold strictly, and the equations deduced in the last paragraph are no longer

* *Ann. de Physik*, **27**, 311 (1908).

strictly applicable. They must, therefore, be replaced by others based on the true equation of condition. In general, however, we do not know the true equation, and we shall, therefore, make use of Van der Waals' equation as a first approximation. Let us first consider the adiabatic change of volume studied by Joule and Thomson in their well-known experiment. Fig. 14 is a diagram of their apparatus. Unit mass of a gas occupying the volume v_1 and under the pressure p_1 flows through a narrow opening into a space in which the pressure is p_2, so that after flowing through the gas occupies the greater volume v_2. An ideal gas would undergo no change in temperature in this process (experiment of Gay-Lussac). Joule and Thomson,* however, observed a slight cooling effect for air and carbon dioxide, and a slight heating effect for hydrogen. They also found that the change in temperature $T_1 - T_2$ was proportional to the difference in pressure $p_1 - p_2$, *i.e.*

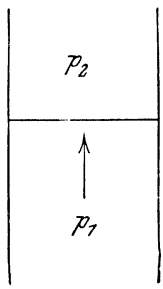


FIG. 14.

$$T_1 - T_2 = k(p_1 - p_2).$$

This result can be deduced from Van der Waals' theory. Since there is no interchange of heat with the surroundings, the change in the total energy of the gas is equal to the work done. Hence

$$-U = w.$$

The work done w is composed of two parts :

(1) The work done by the gas behind the opening $= p_2 v_2$, and

(2) The external work done on the gas in forcing it through $= p_1 v_1$.

Hence $$w = p_2 v_2 - p_1 v_1.$$

Further : $$-U = -\int dU = -\int \frac{\partial U}{\partial T} dT - \int \frac{\partial U}{\partial v} dv.$$

The change in the total energy consists partly of the change in the heat content $c_v(T_2 - T_1)$ and partly of the internal work done in the expansion against the forces acting between the

* A porous plug was used instead of a narrow opening in the actual experiment.

molecules. According to Van der Waals, the pressure p of the gas must be increased by the term $\frac{a}{v^2}$. We may look upon $\frac{a}{v^2}$ as a tension directed towards the interior, and tending to hinder the expansion. The work done against the internal forces when the volume is changed by dv is, therefore, $\frac{a}{v^2}dv$, and the corresponding diminution in energy during the expansion from v_1 to v_2 is:

$$\int_{v_1}^{v_2}\frac{\partial U}{\partial v}dv=\int_{v_1}^{v_2}\frac{a}{v^2}dv=-\frac{a}{v}\left(\frac{1}{v_2}-\frac{1}{v_1}\right).$$

Hence $$-c_v(T_2-T_1)+a\left(\frac{1}{v_2}-\frac{1}{v_1}\right)=p_2v_2-p_1v_1.$$

From Van der Waals' equation

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT,$$

it follows that $$p_1v_1=RT_1-\frac{a}{v_1}+bp_1+\frac{ab}{v_1^2},$$

$$p_2v_2=RT_2-\frac{a}{v_2}+bp_2+\frac{ab}{v_2^2}.$$

Since a and b are very small quantities, we may neglect the terms which contain the product ab. Hence we obtain

$$-c_v(T_2-T_1)=R(T_2-T_1)-2a\left(\frac{1}{v_2}-\frac{1}{v_1}\right)+b(p_2-p_1).$$

Putting $$c_p=c_v+R,$$

and as a first approximation

$$\frac{1}{v_1}=\frac{p_1}{RT_1},\quad \frac{1}{v_2}=\frac{p_2}{RT_2},$$

we obtain, if T_1-T_2 is small compared with T_1,

$$c_p(T_1-T_2)=\left(\frac{2a}{RT_1}-b\right)(p_1-p_2).$$

Using the ordinary units, the right-hand side of this equation would be expressed in litre-atmospheres, and the left in calories.

In the numerical calculation we must, therefore, multiply the right-hand side by the mechanical equivalent of heat, *i.e.* by the number of calories equivalent to 1 l.-atm. We have

$$1 \text{ l.-atm.} = 1000 \times 76 \times 13{\cdot}6 \times 981 = 1{\cdot}01 \times 10^9 \text{ ergs},$$
$$1 \text{ cal.} \quad = 4{\cdot}19 \times 10^7 \text{ ergs},$$

and thus $$1 \text{ l.-atm.} = \frac{1{\cdot}01 \times 10^9}{4{\cdot}19 \times 10^7} = 24{\cdot}1 \text{ cal.}$$

The constant ratio k between the lowering in temperature and the difference in pressure is, therefore,

$$k = \frac{\frac{2a}{RT_1} - b}{c_p} \times 24{\cdot}1.$$

The change in temperature corresponding to a pressure difference of 1 atm. may be calculated from this equation.

(1) For oxygen at 0° C., taking 1 l. as unit of volume, we have (see p. 64) $a = 1{\cdot}36$, $b = 0{\cdot}0316$, $RT = 22{\cdot}4$, and the molecular specific heat $c_p = 6{\cdot}9$. Hence

$$k = \left(\frac{2{\cdot}72}{22{\cdot}4} - 0{\cdot}0316\right) \times \frac{24{\cdot}1}{6\,9} = 0{\cdot}31,$$

and, therefore, $T_2 - T_1 = -0{\cdot}31°$.

Joule and Thomson found for air at zero $-0{\cdot}28°$, which is in good agreement with the calculated value.

(2) For carbon dioxide we have $a = 3{\cdot}61$, $b = 0{\cdot}0428$, $c_p = 8{\cdot}9$,

so that $$T_2 - T_1 = -\left(\frac{7{\cdot}22}{22{\cdot}4} - 0{\cdot}0428\right) \times \frac{24{\cdot}1}{8{\cdot}8} = -0{\cdot}770.$$

In this case the agreement with experiment is not quite so good. Kester* found the temperature depression $T_2 - T_1$ to be $-1{\cdot}19$ for a fall in pressure of 1 atm. at 20° C.

(3) For hydrogen $a = 0{\cdot}19$, $b = 0{\cdot}023$, $c_p = 6{\cdot}8$,

and hence $$T_2 - T_1 = -\left(\frac{0{\cdot}38}{22{\cdot}4} - 0{\cdot}023\right) \frac{24{\cdot}1}{6{\cdot}8} = +0{\cdot}02.$$

In agreement with this, Joule and Thomson observed a slight rise in temperature for hydrogen. This striking result is due

* *Phys. Zeit. Schr.* **6**, 44 (1905).

to the fact that the work done against the internal forces of attraction is more than compensated in the case of hydrogen by the gain in external work ($p_1v_1 - p_2v_2$). For hydrogen, unlike most other gases, the product pv increases with the pressure (see p. 61), so that $p_2v_2 < p_1v_1$. The only other gas which behaves like hydrogen in this way is helium, which must, therefore, also show a positive "Joule-Thomson effect."

At low temperatures we should have a cooling effect for hydrogen also. From the equation

$$k = \left(\frac{2a}{RT} - b\right) \times \frac{24{\cdot}1}{c_p},$$

it follows that the temperature of this "point of inversion" at which the value of k changes sign and therefore vanishes, is

$$T_0 = \frac{2a}{Rb}.$$

Since $2a = 0{\cdot}38$, $b = 0{\cdot}023$, and $R = 0{\cdot}082$,* we have

$$T_0 = \frac{0{\cdot}38}{0{\cdot}082 \times 0{\cdot}023} = 200^\circ \text{ abs.} = -73^\circ \text{ C.}$$

Olczewski found, in fact, that below -80° hydrogen becomes cooler on expansion, like other gases. For air and hydrogen, therefore, Van der Waals' equation is in quantitative agreement with the Joule-Thomson effect. For carbon dioxide the agreement is only qualitative. The other gases which become cooler by expansion at ordinary temperatures must behave at higher temperatures like hydrogen at the ordinary temperature, *i.e.* on expansion their temperature must also rise. The inversion point at which the Joule-Thomson effect changes sign and, therefore, becomes zero, may be calculated for these gases also. For oxygen we have

$$T_0 = \frac{2a}{Rb} = \frac{2{\cdot}72}{0{\cdot}031 \times 0{\cdot}082} = 1065^\circ \text{ abs.} = 790^\circ \text{ C.}$$

For CO_2,

$$T_0 = \frac{2a}{Rb} = \frac{7{\cdot}22}{0{\cdot}043 \times 0{\cdot}082} = 2050^\circ \text{ abs.} = 1800^\circ \text{ C.}$$

* In litre-atmospheres. Cf. p. 59.

Joule and Thomson carried out experiments at high temperatures, and were able to observe a diminution in the cooling effect. It is probable that the inversion point would be reached at lower temperatures than we should expect from Van der Waals' equation.

It is necessary to define the conception of the inversion temperature a little more closely. In the literature of the subject we find this term used with two distinct meanings: first, as the temperature at which the Joule-Thomson effect vanishes when the gas is allowed to expand from a high pressure p to the pressure of the atmosphere, and, secondly, as the temperature at which the differential coefficient $\frac{dT}{dp}$ vanishes. These two temperatures are not identical, as the experiments of Olczewski * and the theoretical considerations of Porter † have shown.

The machines devised by Linde and Hampson for liquefying air and other permanent gases are based on the Joule-Thomson effect. Air at a high pressure (200 atm.) is allowed to escape through a valve whereby it is cooled very considerably. The air which has been cooled in this way is used in turn to cool the compressed air. On frequent repetition of this process, the temperature of the air ultimately falls to below its boiling point. Work is done against the pressure of the atmosphere only when the expanded air escapes into the atmosphere. The external work may, however, generally be neglected in comparison with the work done against the internal molecular forces, especially at low temperatures.

It is, therefore, easy to understand why all attempts to liquefy hydrogen in Linde's machine were unsuccessful. At the ordinary temperature, hydrogen, unlike air, becomes warm when allowed to expand without doing work. If, however, we cool the compressed hydrogen to below the inversion temperature ($-80°$) before allowing it to expand, its temperature falls when the pressure is released, and by repeated compression and expansion it may be liquefied and even solidified. In machines for liquefying hydrogen it is, therefore, necessary to cool the gas

* *Phil. Mag.* (1907, 6, **13**, 722). † *Ibid.* (1906).

previously with liquid air. Helium, which behaves like hydrogen in this respect, has recently been liquefied in the same way.

4. Change of state.

Fusion of solids. As the temperature is constant during the process of fusion, the fundamental equation (1), p. 83, assumes the form

$$dQ = \frac{\partial U}{\partial v} dv + p\, dv.$$

For 1 gr. of substance the change of volume dv on fusion is equal to the difference between the specific volumes in the solid and liquid states, $dv = v_{\text{liq.}} - v_{\text{sol.}}$. Writing w for the amount of heat necessary to melt 1 gr. of the substance (as on p. 43), we have

$$w = \int_{v_{\text{sol.}}}^{v_{\text{liq.}}} \frac{\partial U}{\partial v} dv + p(v_{\text{sol.}} - v_{\text{liq.}}).$$

The integral is the change of internal energy produced by the fusion of unit mass, or the "internal latent heat of fusion" w'. In general the difference between the total heat of fusion and w' is a small quantity, as the change in volume on melting is very small.

The following example will illustrate this. For water we have $w = 80$ cal. 1 gr. of ice contracts on melting by 0·09 c.c., so that the difference $v_{\text{liq}} - v_{\text{sol.}} = -0{\cdot}09$ c.c. If the fusion takes place at atmospheric pressure, the work done is therefore

$$p(v_{\text{liq.}} - v_{\text{sol.}}) = -\frac{0{\cdot}09}{1000} \text{ litre-atmospheres}$$

$$= -\frac{0{\cdot}09 \times 24{\cdot}1}{1000} = 0{\cdot}0022 \text{ cal.}$$

It is therefore quite negligible in comparison with the total latent heat.

The latent heat of fusion w depends on the temperature at which the melting takes place. It will be shown later on that the melting point is determined by the pressure under which the substance is fused. By altering the pressure, we can therefore cause the substance to fuse at different temperatures. With the aid of the law of the conservation of energy, we can calculate the relationship between the latent heat w and the

melting point T as follows: Let w be the latent heat for 1 gr. at the temperature T, and at the higher temperature $T+dt$ let the latent heat be $w+dw$. If c_1 is the specific heat of the solid and c_2 that of the liquid, we may imagine the change from solid at the temperature T to liquid at the temperature $T+dT$ to take place in two different ways as follows:

1. The substance is melted at the temperature T, and the liquid is then heated from T to $T+dT$. The heat absorbed in this process is $w+c_2dT$.

2. The pressure on the solid is altered at the temperature T until it has attained the value which corresponds to the higher melting point $T+dT$. The solid is then heated to $T+dT$ and melted at this temperature. The heat absorbed is then

$$c_1dT+w+dw.$$

As the work done in consequence of the change in volume is very small in both cases, we may neglect it in comparison with the change of energy due to the absorption of heat, and since (by the law of conservation) the change in energy is independent of the way in which the change is produced, we obtain, by equating the heats absorbed in both cases,

$$w+c_2dT=c_1dT+w+dw \quad \text{or} \quad \frac{dw}{dT}=c_2-c_1. \quad \ldots\ldots\ldots(1)$$

The latent heat must therefore increase with the temperature for all substances, since the specific heat of the liquid c_2 is found by experiment to be greater in all cases than that of the solid c_1.* Pettersen finds for water:

$T=$	$-2\cdot8°$	$-5\cdot0°$	$-6\cdot5°$ C.
$w=$	77·85	76·75	76·00

From these figures we derive $\frac{dw}{dT}=0\cdot50$. The direct determination gives $c_2-c_1=0\cdot498$, an excellent confirmation of the theory.

Evaporation. For the evaporation of unit mass of a liquid, we have the equation

$$\lambda=\lambda'+p(v_2-v_1). \quad \ldots\ldots\ldots(2)$$

*The theoretical deduction of this experimental fact will be given in the last chapter.

Here λ is the total quantity of heat necessary for the volatilisation of unit mass at the temperature T, p is the pressure of the saturated vapour against which the evaporation takes place, v_2 and v_1 are the specific volumes of the vapour and the liquid respectively, and λ' is the internal heat of evaporation, *i.e.* the difference between the total heat absorbed and the work done during evaporation. In other words, λ' is the increase in internal energy during evaporation. As the specific volume of the gas is always greater than that of the liquid, λ' is $<\lambda$ in general by a quantity which cannot be neglected.

Equation (2) can be simplified very considerably when p is small. At low pressures the specific volume of the vapour is large compared with that of the liquid, so that $p(v_2-v_1)$ is nearly equal to $p \cdot v_2$. Further, if we assume that the vapour obeys the simple gas laws, we have $pv=\frac{RT}{M}$, where M is the molecular weight of the vapour. Hence

$$\lambda=\lambda'+\frac{RT}{M},$$

and for the molecular heat of evaporation $L=M\lambda$:

$$L=L'+RT.$$

We can calculate the relationship between temperature and heat of evaporation from considerations similar to those employed in the deduction of the relationship between temperature and heat of fusion.

Let unit mass of the substance be made to go from temperature T, and vapour pressure p to temperature $T+dT$, and the corresponding vapour pressure $p+dp$. This change of state can take place in two ways :

I. (*a*) Let 1 gr. of the liquid evaporate at the constant temperature T and under the pressure p of the saturated vapour. In this process the quantity of heat λ is absorbed, and work $p(v_2-v_1)$ is done by the substance. v_1 and v_2 are the specific volumes of gas and liquid under the given conditions.

(*b*) The vapour is now heated by dT at the constant pressure p. Here heat absorbed $=c_p\,dT$, and work done $=p\frac{\partial v_2}{\partial T}dT$. (The

change in volume of the vapour dv_2 corresponding to a simultaneous change in pressure and temperature is the sum of the quantities $\frac{\partial v_2}{\partial T}dT$ and $\frac{\partial v_2}{\partial p}dp$, which are the changes in volume at constant pressure and constant temperature respectively.)

(*c*) The vapour is now compressed isothermally at $T+dT$ until the pressure is $p+dp$.

Here heat absorbed = work done $= p\frac{\partial v_2}{\partial p}dp \quad (<0)$.

The total heat absorbed is therefore

$$Q_{\mathrm{I}} = \lambda + c_p dT + p\frac{\partial v_2}{\partial p}dp,$$

and the corresponding work done :

$$w_1 = p(v_2 - v_1) + p\left(\frac{\partial v_2}{\partial T}dT + \frac{\partial v_2}{\partial p}dp\right).$$

Hence the change in energy :

$$U_1 = Q_1 - w_1 = \lambda + c_p dT - p(v_2 - v_1) - p\frac{\partial v_2}{\partial T}dT. \quad \ldots\ldots(3)$$

II. (*a*) The liquid is heated by $dT°$ at the higher pressure $p+dp$. Heat absorbed $= c_1 dT_1$, work done $= 0$, if c_1 be the specific heat of the liquid and the slight expansion on heating be neglected.

(*b*) Evaporation at $T+dT$ and $p+dp$.

Heat absorbed $= \lambda + d\lambda$, work done $= (p+dp)(v_2+dv_2-v_1)$, since the volume of the vapour at $T+dT$ and $p+dp$ is v_2+dv_2.

Hence
$$Q_{\mathrm{II}} = c_1 dT + \lambda + d\lambda,$$
$$w_{\mathrm{II}} = (p+dp)(v_2+dv_2-v_1),$$

and $U_{\mathrm{II}} = Q_{\mathrm{II}} - w_{\mathrm{II}} = c_1 dT + \lambda + d\lambda - (p+dp)(v_2+dv_2-v_1)$. ...(4

By the law of the conservation of energy $U_{\mathrm{I}} = U_{\mathrm{II}}$, since the change in energy must be independent of the way in which the system passes from the initial to the final state. We thus obtain from (3) and (4) :

$$\left.\begin{aligned} d\lambda &= c_p dT - c_1 dT + p\,.\,dv_2 - p\frac{\partial v_2}{\partial T}dT + dp\,dv_2 + dp(v_2 - v_1) \\ &= c_p dT - c_1 dT + p\frac{\partial v_2}{\partial p}dp + dp(v_2 - v_1), \end{aligned}\right\} \quad (5)$$

since $dp_2 dv_2$ is of the second order of magnitude and may be neglected.

The quantity $c_p dT + p\frac{\partial v_2}{\partial p} dp$ is therefore the amount of heat which the saturated vapour must absorb in passing from temperature T (and pressure p) to temperature $T+dT$ (and pressure $p+dp$). We may write this quantity $= c_y dT$, and call the quantity

$$c_y = c_p + p\frac{\partial v_2}{\partial p} \cdot \frac{dp}{dT}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

the *specific heat of the saturated vapour.*

The temperature coefficient of the heat of evaporation is then, by (5) and (6),

$$\frac{d\lambda}{dT} = c_y - c_1 + \frac{dp}{dT}(v_2 - v_1). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

We see at once that the specific heat of a saturated vapour may be negative. The second term of (6) is always <0, since $\frac{\partial v_2}{\partial p}$ is negative, and hence $c_y < 0$ also, if $-p\frac{\partial v_2}{\partial p} \cdot \frac{dp}{dT} > c_p$. According as $c_y \gtrless 0$, we have three distinct classes of saturated vapours.

I. $c_y > 0$. If we compress the vapour and wish it to remain saturated, we must abstract heat. If we do not abstract heat, but compress the vapour adiabatically, part of the vapour will condense. On the other hand, if we expand the vapour adiabatically it will become unsaturated.

II. $c_y < 0$. If the vapour is to remain saturated during compression, we must withdraw heat from it. An adiabatic compression will, therefore, cause the vapour to become unsaturated or "superheated," an adiabatic expansion will produce partial condensation.

III. $c_y = 0$. The vapour will remain saturated on adiabatic compression or expansion.

We can simplify equations (6) and (7) very materially, by considering evaporation at so low a temperature that we may assume the validity of the simple gas laws at least approximately. It then follows, since $v_2 = \frac{RT}{Mp}$, that

$$\frac{\partial v_2}{\partial p} = -\frac{RT}{Mp^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

and combining (6) and (8), we obtain

$$c_q = c_p - v_2 \cdot \frac{dp}{dT}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Further, if we neglect v_1 in comparison with v_2, which is always permissible when the vapour pressure is small, we may transform (7) into

$$\frac{d\lambda}{dT} = c_p - c_1, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

an equation identical in form with equation (1) on page 103, which gives the variation of the latent heat of fusion with the temperature.

For the internal heat of evaporation we have the equation

$$\lambda' = \lambda - p(v_2 - v_1),$$

and hence
$$\frac{d\lambda'}{dT} = \frac{d\lambda}{dT} - p\frac{d(v_2 - v_1)}{dT} - (v_2 - v_1)\frac{dp}{dT},$$

and by (7),
$$\frac{d\lambda'}{dT} = c_q - c_1 - p\frac{d(v_2 - v_1)}{dT}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

Again applying the gas laws for the saturated vapour and neglecting v_1 in comparison with v_2, we obtain from (9) and (11):

$$\left.\begin{aligned}\frac{d\lambda'}{dT} &= c_p - v_2\frac{dp}{dT} - p\frac{dv_2}{dT} - c_1 = c_p - \frac{d(pv_2)}{dT} - c_1 \\ &= c_p - \frac{R}{M} - c_1 = c_v - c_1.\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

From (7) and (11) it follows that $\frac{d\lambda}{dT}$ and $\frac{d\lambda'}{dT}$ might formally be either positive or negative. At higher temperatures and vapour pressures, however, both coefficients must be negative, since the heats of evaporation vanish at the critical point. At this temperature liquid and vapour become identical, and their internal energies are equal. We have, further, $\frac{d\lambda}{dT} = \frac{d\lambda'}{dT} = 0$, as the specific volumes and the specific heats of both states are equal to one another. The temperature coefficients of the heats of evaporation, therefore, gradually become zero as we approach the critical temperature.

From equation (9) it is easy to calculate that the specific heat of saturated water vapour, for example, is negative at the normal boiling point. Thus for 1 gr. of water vapour at 100° C., we have

$$c_p = 0{\cdot}45 \text{ cal.},$$

$$v_2 = 1{\cdot}650 \text{ litre, and}$$

$\frac{dp}{dT}$ (increase in vapour pressure for an increase in temperature from 100° to 101° C.) = 0·042 atm.

Hence

$$v_2 \frac{dp}{dT} = 0{\cdot}0694 \text{ litre-atmosphere} = 0{\cdot}0694 \times 24{\cdot}1 = 1{\cdot}67 \text{ cal.},$$

and $c_v = 0{\cdot}45 - 1{\cdot}67 = -1{\cdot}2$ cal.

By the compression of 1 gr. of saturated water vapour at 100° to saturated water vapour at 101°, we have an emission of 1·2 cal. If this heat is not allowed to escape, we do not obtain saturated water vapour at 101°, but superheated steam at a correspondingly higher temperature. Conversely, if we allow saturated water vapour to expand adiabatically, condensation takes place. We may mention that this spontaneous condensation of water vapour, which for a slight expansion takes place only in the presence of dust particles or ions, has been successfully employed in counting the number of ions or nuclei in the vapour.

If we wished to perform determinations of this sort with a liquid whose saturated vapour had a positive specific heat, we should have to expand the vapour adiabatically instead of compressing it.

5. Thermo-chemistry.

Thermo-chemical nomenclature. In the previous paragraph we have discussed the changes of state which can be produced in a substance of uniform composition by the action of heat and pressure. We may characterise such so-called " physical " processes by the statement that the energy changes in the body depend essentially on the variations in temperature, pressure, and volume during the process. We distinguish such processes

from "chemical" processes, in which the energy change of the system depends essentially on changes in the nature of the component substances. For example, if we heat a mixture of hydrogen and oxygen, the energy of the gaseous mixture increases at low temperatures according to laws which apply to all gases alike. At a certain temperature, however, generally called the ignition temperature, chemical combination begins with formation of water and violent evolution of heat. The energy of the system decreases, therefore, by the amount of heat given out to the surroundings during the reaction. This is also true for a system, such as a mixture of iron and sulphur, which consists only of solid substances. At higher temperatures these substances unite with evolution of heat to form sulphide of iron. The energy content of the sulphide must therefore be less than that of the mixture of iron and sulphur.

The change in the internal energy consequent on a chemical reaction depends also, by the first law, on the variations in temperature and volume which the system undergoes. The heat evolved may be used up partly in raising the temperature of the system and in doing external work. The remainder is given out to the surroundings. If we wish to measure the total energy change accompanying a chemical transformation, we must keep the temperature and volume constant during the reaction. The heat evolved is then an exact measure of the decrease in the internal energy of the reacting substances. The amount of heat given out at constant volume and temperature during a chemical reaction is called the *heat of reaction* Q. Reactions are called exothermic when heat is given out to the surroundings. In this case Q is reckoned positive. Reactions which are accompanied by an absorption of heat are called endothermic reactions, and are characterised by negative values of Q.

The heat of reaction is proportional to the quantity of the reacting substances. It is customary to designate as heat of reaction the amount of heat which is evolved during the transformation of 1 gram molecule of the reacting substances. If the molecular weight is unknown, as is the case for solids and liquids, it is usual to take as unit of mass the number of grams

which is equal to the formula weight of the substance. Thus 18,400 cal. are evolved when 207 grams of lead combine with 32 grams of sulphur, and this quantity is called the heat of reaction, or also the heat of formation of lead sulphide. Thermochemistry is concerned with the determination of heats of reaction.

The results of thermo-chemical measurements are expressed in the form of equations. On the left-hand side of the equation we write the chemical symbols of the reacting substances, and, on the right hand, the symbols of the products of reaction plus or minus the heat of reaction according as the reaction is exothermic or endothermic.

Thus, for the formation of lead sulphide we have the equation

$$Pb + S = PbS + 18400 \text{ cal.}$$

As an example of an endothermic reaction, we may take the formation of hydrogen iodide according to the equation

$$I_2 + H_2 = 2HI - 6000 \text{ cal.}$$

The heat of formation of one gram molecule of HI is, therefore,

$$-\frac{6000}{2} = -3000 \text{ cal.}$$

When there is no doubt as to the formula of the product of the reaction, we may often make use of a contracted notation, viz.

$$(Pb, S) = +18400 \text{ cal.},$$

or

$$(H_2, I_2) = -6000 \text{ cal.}$$

The above-mentioned condition that the heat of reaction is to be measured at constant volume is generally difficult to realise experimentally. If there be a change in volume during the reaction, work will be done in overcoming the pressure on the system. This amount of work w is positive when the volume increases and negative when the volume diminishes. If we denote by Q the heat of reaction measured in an open vessel, that is at constant pressure, the change in energy is equal to the heat evolved plus the work done, so that

$$Q = Q_p + w.$$

For reactions in which only solids and liquids take part, the change in volume, and therefore the work done, is generally very small and negligible compared with Q. In this case we may put $Q = Q_p$ with a high degree of approximation. For reactions in which gases or vapours take part, the change in volume may, however, be considerable. If p be the constant pressure at which the reaction takes place, v the volume of a gram molecule of a gas at this pressure and the temperature T of the reaction, and if ν be the number of gram molecules by which the gaseous substances increase during the reaction, the work done during the reaction is $A = \nu pv$, where ν may be either positive or negative. If the simple gas laws hold for the reacting gases, we have, for every gram molecule, $pv = RT$, and hence

$$Q = Q_p + \nu RT.$$

For example, in the above-mentioned case of the formation of hydrogen iodide we have $\nu = 1$, as the equation applies to the combination of hydrogen with solid iodine. For the formation of steam from hydrogen and oxygen,

$$(2H_2 + O_2 = 2H_2O) \quad \nu = -1,$$

for the formation of liquid water $\nu = -3$, and so on. In many cases, however, the quantity νRT is much smaller than Q or Q_p, so that for approximate calculations we may take these quantities to be equal to one another.

The internal energy of a substance is different according as it is in the solid, liquid, or gaseous state. As both fusion and evaporation require absorption of heat, all substances must be richer in energy in the gaseous state than in the liquid state, and in the liquid state again they must contain more energy than in the solid state. The heat of reaction will, therefore, vary according as the reacting substances are solid, liquid, or gaseous, and we must specify the states of the reacting substances in our thermo-chemical equation whenever they are not self-evident. The state of the reacting substances is self-evident in the case of the formation of lead sulphide, as all the substances concerned are solid at ordinary temperatures for a considerable range of temperature. This is not the case, however, for the formation of hydrogen iodide. For the reaction between

gaseous iodine and hydrogen we should therefore write the equation

$$H_2 + I_2 \text{ (gas)} = 2HI + Q_1.$$

As I_2 (solid) contains less energy than I_2 (gas), $+Q_1$ must be greater than -6000 cal. This is, in fact, the case. So much so that the heat of reaction is positive, *i.e.* the combination of the gaseous elements is accompanied by an evolution of heat.

For the formation of water we have, for example, the following equations :

1. Formation of steam,

$$2H_2 + O_2 = 2H_2O \text{ (gas)} + 118000 \text{ cal.}$$

2. Formation of liquid water,

$$2H_2 + O_2 = 2H_2O \text{ (liq.)} + 137000 \text{ cal.}$$

The difference of 19000 cal. corresponds to the heat of evaporation which is evolved when 2 mols. of steam are condensed to 2 mols. of liquid water.

In order to avoid the cumbersome notation H_2O (liq.), I_2 (solid), etc., various abbreviations have been proposed. Pfaundler recommends a line under the formula to denote the solid state, and a line over the formula to denote the gaseous state.* It may serve as a mnemonic that solids generally sink downwards, while gases as a rule rise upwards. Thus ice would be written $\underline{H_2O}$, water H_2O, and steam $\overline{H_2O}$. These symbols are, of course, only necessary in cases of doubt. Thus the line over H_2 or O_2 is superfluous, unless we happened to be considering reactions at exceedingly low temperatures. When necessary, we shall make use of Pfaundler's symbols in the following.

The solution of a substance in a liquid is also generally accompanied by the evolution (or absorption) of an amount of heat, which is spoken of as the *heat of solution.*

The value of the heat of solution is dependent on the amount of solvent in which unit mass of the substance is dissolved. Experiment has shown, however, that the heat of solution is independent of the concentration when the solution formed is

* Müller-Pouillet, 10th edition, vol. iii. p. 555.

very dilute. The heat evolution on further dilution of a very dilute solution is practically negligible, and it is therefore usual to use the term heat of solution to denote the heat evolved (or absorbed) in the formation of a very dilute solution. The solution of a substance may be written as a thermo-chemical equation, *e.g.* $NaCl + H_2O = NaCl\ aq. + Q$ cal.

H_2O represents a very large number of mols. of water, and the resulting dilute solution is represented by NaCl aq.

The heat evolved in a chemical reaction will therefore vary according as the reacting substances are in solution or not. Thus the formation of solid ammonium chloride from gaseous ammonia and gaseous hydrochloric acid has not the same heat of reaction as the formation of ammonium chloride solution from aqueous ammonia and aqueous hydrochloric acid. We must specify the state of solution in our thermo-chemical equations. The above example must be written either

$$\overline{NH_3} + \overline{HCl} = \underline{NH_4Cl} + Q \text{ cal.}$$

or $$NH_3\ aq. + HCl\ aq. = NH_4Cl\ aq. + Q' \text{ cal.}$$

The fundamental law of thermo-chemistry was discovered in 1840 by Hess. This law states that the heat of formation of a compound is the same whether the compound be formed directly from the elements, or indirectly in any way whatever. Lead sulphate, for example, may be prepared in two different ways as follows :

1.
$$\begin{aligned} Pb + S &= PbS + Q_1 \\ PbS + 2O_2 &= PbSO_4 + Q_2 \\ \hline Pb + S + 2O_2 &= PbSO_4 + Q_1 + Q_2 \end{aligned}$$

2.
$$\begin{aligned} Pb + O &= PbO + Q_3 \\ S + O_2 &= SO_2 + Q_4 \\ SO_2 + O &= SO_2 + Q_5 \\ PbO + SO_3 &= PbSO_4 + Q_6 \\ \hline Pb + S + 2O_2 &= PbSO_4 + Q_3 + Q_4 + Q_5 + Q_6 \end{aligned}$$

By the law of Hess we have

$$Q_1 + Q_2 = Q_3 + Q_4 + Q_5 + Q_6.$$

Hess regarded this law as self-evident, and did not consider a proof necessary. It is, however, a consequence of the law of the conservation of energy. For, according to this law, the energy of an initial state (*e.g.* oxygen, lead, sulphur) and of a final state (lead sulphate) is independent of the way in which the change of state (formation of lead sulphate) is produced. It is interesting to note that this law was regarded as self-evident before Mayer had ever formulated or given expression to it.

Any of the calorimeters described in Chapter II. is in principle capable of being used for the determination of heats of reaction. In any actual case it will, of course, be necessary to adapt the apparatus to the purpose which it is intended to serve. Jul. Thomsen, Berthelot, Favre and Silbermann, Stohmann, de Forcrand, Luginin, and of late years Th. W. Richards, Wrede, and W. A. Roth have been the chief workers in the development of thermo-chemistry. The more important of the apparatus devised and used by them are described in detail in many text-books.

Of late, efforts have been made to increase the accuracy of thermo-chemical measurements. The most troublesome error in accurate calorimetry is caused by the interchange of heat with the surroundings.

The graphical method mentioned on p. 16 is inadequate for very accurate determinations. There are essentially three methods which have been devised with a view to avoiding this error. Rumford first determines roughly the rise in temperature Δt produced by the reaction, and cools the calorimeter to $\frac{\Delta t}{2}$ below the temperature of the surroundings before each subsequent determination. When the reaction has taken place, the temperature of the calorimeter is about $\frac{\Delta t}{2}$ higher than the surrounding temperature, and we may assume that the heat absorbed before the reaction and the heat evolved after the reaction approximately compensate one another. Regnault and Pfaundler begin the experiment at room temperature, and observe the alteration in temperature for some time after the reaction has taken place. Assuming that Newton's law holds

for the heat given out to the surroundings during cooling, it is easy to deduce a formula by means of which we may calculate the correction necessary.*

Both methods are inadequate, as Richards has shown. The determinations are more likely to be really accurate when the interchange of heat with the surroundings has been eliminated completely as far as possible. One way of attaining this is to make the vessel in which the reaction takes place as impermeable to heat as possible. Dewar vessels are sufficient in many cases. These are double-walled glass vessels evacuated in the space between the two walls. They are used in all experiments with liquid air. By this device all loss of heat by conduction is prevented, and the loss by radiation can be very much reduced by covering the surface of the glass with a highly reflecting layer of silver. A second method, used by Richards, is to surround the calorimeter with a liquid bath in which the temperature can be regulated during the reaction so as always to be nearly equal to the temperature in the interior of the calorimeter.

We may, for example, surround the calorimeter with a bath of dilute acid and run in alkali from a burette. The rate at which the alkali is added can be regulated so that the heat of neutralisation produces at every instant the same rise in temperature in the bath as is produced by the reaction in the interior of the calorimeter. Richards and his colleagues have made some exceedingly accurate calorimetrical determinations in this way.†

The following table contains the heats of formation of some simple inorganic compounds and also some heats of solution:‡

A. Compounds of Metals.

1. *Oxides.*

$2K+O$	97100	$Fe+O$	64600
$2Na+O$	91000	$Ni+O$	59700
$Ca+O$	145000	$Co+O$	63800
$Ba+O$	133400	$Cu+O$	37200
$Ba+2O$	145500	$2Cu+O$	43800
$Zn+O$	85200	$2Ag+O$	4900–7000

* See Müller-Pouillet, 10th edition, vol. iii. p. 174. Also Ostwald-Luther, *Hilfs- und Handbuch*, 3rd edition, p. 304.

† *Zeitschrift f. physikal. Chemie*, **52**, 551; **59**, 532 (1907).

‡ See Landolt-Börnstein, 3rd edition.

2. *Sulphides.*

$2K+S$	103500
$2Na+S$	88200
$Ca+S$	92000
$Ba+S$	102500
$Zn+S$	$<$ 43000
$Fe+S$	$<$ 24000
$Ni+S$	$<$ 19400
$Co+S$	$<$ 21700
$2Cu+S$	20300
$2Ag+S$	3000~5300

3. *Chlorides.*

$K+Cl$	105600
$Na+Cl$	97800
$Ca+2Cl$	169800
$Ba+2Cl$	196900
$Zn+2Cl$	97300
$Fe+2Cl$	82100
$Ni+2Cl$	74500
$Co+2Cl$	76500
$Cu+2Cl$	51500
$Cu+Cl$	35400
$Ag+Cl$	29200

4. *Bromides.*

$K+Br$ (liq.)	95450
$Na+Br$	85900
$Ca+2Br$	140850
$Ba+2Br$	172100
$Zn+2Br$	76000
$Fe+2Br+aq.$	78100
$Ni+2Br+aq.$	71800
$Co+2Br+aq.$	72900
$Cu+2Br$	32600
$Cu+Br$	25000
$Ag+Br$	23400

5. *Iodides.*

$K+I$	80100
$Na+I$	69100
$Ca+2I$	107250
$Ba+2I$	149700
$Zn+2I$	49200
$Fe+2I+aq.$	47650
$Ni+2I+aq.$	41400
$Co+2I+aq.$	42000
$Cu+I$	16750
$Ag+I$	14000

B. Compounds of Non-Metals.

$\overline{H}+\overline{F}=\overline{HF}$	38500
$\overline{H}+\overline{Cl}=\overline{HCl}$	22000
$\overline{H}+Br=\overline{HBr}$	8500
$\overline{H}+\underline{I}=\overline{HI}$	6150
$2\overline{H}+\overline{O}=\overline{H_2O}$	58000
$2H+2O+aq.=H_2O_2+aq.$	45300
$2\overline{H}+\underline{S}\,(rh.)=\overline{H_2S}$	2700
$3\overline{H}+\overline{N}=\overline{NH_3}$	12000
$\overline{H}+3\overline{N}+aq.=NH_3aq.$	$-$61600
$3\overline{H}+\underline{As}=\overline{A_3H_3}$	$-$36700
$3\overline{H}+\underline{Sb}=SbH_3$	$-$86800
$4\overline{H}+C=\overline{CH_4}$ (Diamond)	$+$18900
$4\overline{H}+Si=\overline{SiH_4}$	24800
$Br+\overline{Cl}=BrCl$	700

$\underline{I}+\overline{Cl}=ICl$	5800
$\underline{I}+3\overline{Cl}=\underline{ICl_3}$	21500 15500
$\underline{I}+Br=IBr$	2500
$2\underline{S}+2\overline{Cl}=S_2Cl_2$	14300
$2\underline{S}+2Br=S_2Br_2$	2000
$2\underline{S}+2\underline{I}=2\underline{SI}$	0
$\underline{P}+3\overline{Cl}=PCl_3$	76000
$\underline{P}+3Br=PBr_3$	44800
$\underline{P}+3\underline{I}=\underline{PI_3}$	10900
$\underline{B}+3\overline{Cl}=\underline{BCl_3}$	89100
$\underline{B}+3\overline{F}=\underline{BF_3}$	234800
$\underline{C}+4\overline{Cl}=\underline{CCl_4}$	21000
$Si+4\overline{Cl}=\underline{SiCl_4}$	121800

$Si+4Br=SiBr_4$	71000	$2\overline{N}+3\overline{O}=\overline{N_2O_3}$	−21400
$Si+4I=SiI_4$	6700	$\overline{N}+2\overline{O}=\overline{NO_2}$	−7600
$2\overline{Cl}+\overline{O}=\overline{Cl_2O}$	−17000	$2\overline{N}+5\overline{O}=\overline{N_2O_5}$	−1200
$2I+5\overline{O}=I_2O_5$	48000	$2As+3\overline{O}=As_2O_3$	154700
$S+2\overline{O}=\overline{SO_2}$	70000	$2B+3\overline{O}=B_2O_3$	272600
$S+3\overline{O}=\overline{SO_3}$	91900	$C+\overline{O}=\overline{CO}$	29000
$SO_3+H_2O=H_2SO_4$	21300	amorph $C+2\overline{O}=CO_2$	96000
$2\overline{N}+\overline{O}=N_2O$	−20600	amorph $Si+2\overline{O}=\overline{SiO_2}$	184500
$N+\overline{O}=\overline{NO}$	−21600	amorph	

HEATS OF SOLUTION OF METALLIC COMPOUNDS.

Substance.	(Dissolved in) mols. H_2O.	Q	Substance.	(Dissolved in) mols. H_2O.	Q
LiOH	400	5800	NaI	200	1200
NaOH	200	9900	KI	200	−5100
KOH	250	13300	NH_4I	200	−3550
$KOH.2H_2O$	170	−30	CaI_2	400	27700
LiCl	230	8440	BaI_2	∞	10300
NaCl	100	−1200	$BaI_2.H_2O$	500	−6850
KCl	200	−4400	ZnI_2	400	11300
NH_4Cl	200	−4000	$LiNO_3$	100	300
$CaCl_2$	300	17400	$NaNO_3$	200	−5000
$CaCl_2.6H_2O$	400	−4340	KNO_3	200	−8500
$BaCl_2$	400	−2100	NH_4NO_3	200	−6320
$BaCl_2.2H_2O$	400	−4900	$Ca(NO_3)_2$	400	3950
$ZnCl_2$	300	15600	$Ca(NO_3)_2.4H_2O$	400	−7250
$FeCl_3$	350	17900	$Ba(NO_3)_2$	400	−9400
$FeCl_3.4H_2O$	400	2750	$Zn(NO_3)_2.6H_2O$	400	−5840
$CuCl_2$	600	11000	$Cu(NO_3)_2.6H_2O$	400	−10700
$CuCl_2.2H_2O$	400	4200	Li_2SO_4	200	6050
LiBr	∞	11350	Na_2SO_4	400	400
NaBr	200	−190	$Na_2SO_4 10H_2O$	400	−18800
KBr	200	−5100	K_2SO_4	100	−6580
NH_4Br	200	−4400	$(NH_4)_2SO_4$	400	−2400
$CaBr_2$	400	24510	$CaSO_4$	∞	4400
$CaBr_2.6H_2O$	400	−1100	$CaSO_4.2H_2O$	∞	−300
$BaBr_2$	400	5000	$ZnSO_4$	400	18400
$BaBr_2.2H_2O$	400	−4100	$ZnSO_4.7H_2O$	400	−4260
$ZnBr_2$	400	15000	$FeSO_4.7H_2O$	400	−4500
$CuBr_2$	∞	7900	$CuSO_4$	400	15800
$CuBr_2.4H_2O$	∞	−1500	$CuSO_4 5H_2O$	400	−2750
LiI	∞	14900			

HEATS OF DILUTION AND HEATS OF SOLUTION OF ACIDS.

Mols. of water to 1 mol. acid.	H_2SO_4	HCl	HNO_3	H_3PO_4	$C_2H_2O_2$
1	+6380	5370	3340	1740	−152
2	9420	11360	4860	—	−156
5	13110	14960	6600	—	—
8	—	—	7220	—	—
10	14950	16160	7270	4600	—
20	16260	16760	7360	—	+173
50	16700	17100	—	—	+278
100	16900	17200	7210	5270	+335
200	17100	—	7180	5350	+375
300	—	17300	—	—	—
800	17600	—	—	—	—
1600	17900	—	—	—	—

HEATS OF DILUTION OF BASES.

Mols. H_2O added.	To $KOH + 3H_2O$.	To $NaOH + 3H_2O$.
2	1500	2130
4	2100	2890
6	2360	3100
17	2700	3080
47	2740	3100
97	2750	3000
197	2750	2940

Summarising the results given in the above tables, we may say that elements at opposite ends of the periodic system combine with great evolution of heat, *e.g.* the alkalies and the alkaline earths with the halogens and oxygen. In the formation of similar types of compounds, such as oxides, chlorides, sulphides, etc., the heat of formation generally diminishes in the same sequence as the atomic weight increases. It also runs parallel with the tendency to form ions (electro-affinity).* The elements which have a strong tendency to form cations (*e.g.* potassium and sodium), and also those which have a strong tendency to form anions (such as chlorine), give par-

* See Abegg and Bodländer, *Zeit. f. anorg. Chem.* **20**, 453 (1899).

ticularly large heats of formation with elements which are opposite to them in electrical character. Elements which are similar in chemical character, such as iron, nickel, and cobalt, are also similar in their thermo-chemical behaviour. When elements in the same vertical column of the periodic system combine with one another, the heat of reaction is greater the further they are apart. In compounds of the same two elements in different atomic proportions, the first step corresponds to the greatest heat of formation (*e.g.* $CuCl \rightarrow CuCl_2$, $BaO \rightarrow BaO_2$, $SO_2 \rightarrow SO_3$, $ICl \rightarrow ICl_3$), but there are exceptions to this rule (*e.g.* $CO \rightarrow CO_2$).

The marked influence which the electro-affinity of an element has on the heat of formation of its compounds is illustrated by the diagram (Fig. 15) which is due to van't Hoff. The heats of reaction of sodium and chlorine in their compounds with S, O, Cl, I, H, and Na are plotted as ordinates. The heats of formation of the sodium compounds diminish in approximately the same sequence as those of the chlorine compounds increase.*

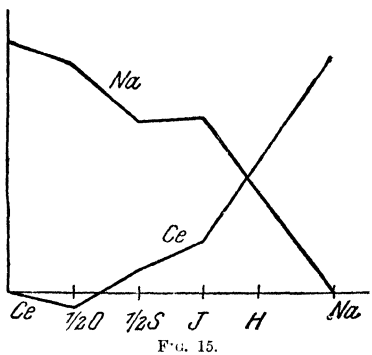


FIG. 15.

Comparing the heats of solution with one another, we see that anhydrous salts, which can be in equilibrium with their saturated solutions at the ordinary temperature, generally dissolve with absorption of heat, while anhydrous salts, which can form hydrates, generally dissolve with evolution of heat, as their heats of hydration are for the most part very great.

Some salts, however, in spite of great similarity in their chemical composition and behaviour, have remarkably divergent heats of solution (*e.g.* $Na_2SO_4 + 400$ cal., $K_2SO_4 - 6580$ cal., $LiBr + 11350$ cal., $NaBr - 190$ cal., etc.).

The heats of neutralisation of dilute acids and bases, determined by Thomsen, Berthelot, and others, are worthy of special notice. The figures given in the following table are for each

* *Vorlesungen*, iii. p. 85.

acid almost entirely independent of the nature of the base. They are dependent on the nature of the acid in so far as they are the same for nitric and hydrochloric acids, greater for sulphuric acid, and less for carbonic acid.

Base.	HCl	HNO_3	$\frac{1}{2}H_2SO_4$	$\frac{1}{2}H_2CO_3$
LiOH - - -	13850	—	15645	—
NaOH - - -	13700	13700	15690	10200
KOH - - -	13700	13800	15645	10100
TlOH - - -	13740	—	15650	—
$\frac{1}{2}Ca(OH)_2$ - - -	14000	13900	15570	—
$\frac{1}{2}Ba(OH)_2$ - - -	13850	13900	—	—

The explanation of this striking regularity follows at once from the theory of electrolytic dissociation. According to this theory the neutralisation of a strong base with a strong acid is due simply to the combination of $H^{\cdot}$ and OH' ions to form undissociated water according to equations such as

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O.$$

When this is the case, the heat of reaction must be quite independent of the nature of the anion and of the cation, as these are not affected by the reaction. This is clearly true for nitric and hydrochloric acids with all the bases given in the table. For sulphuric and carbonic acids, however, the conditions for the validity of the theory are apparently not fulfilled. In the first case, the heat of dilution of sulphuric acid amounts to 2000 cal., and this amount must be subtracted from the figure given in the table, as it is evolved when the alkali and acid are mixed. In the second case, carbonic acid is so weak an acid that it is practically undissociated. The heat necessary for the dissociation into ions therefore uses up part of the heat of neutralisation. From the table it follows that the electrolytic dissociation of $\frac{1}{2}$ mol. H_2CO_3 requires $13700 - 10200 = 3500$ calories. The constant heat of neutralisation 13700 cal. is the heat of ionisation of water, *i.e.* the quantity of heat required for the dissociation of water, and liberated on the combination of its ions.

According to recent experiments by Woermann * this heat of neutralisation is slightly greater for dilute solutions of KOH than for NaOH. Woermann gives the following heats of neutralisation at 0° C. (ice calorimeter):

$$\begin{aligned} HCl + NaOH &= 14620 \text{ cal.} \\ HCl + KOH &= 14755 \text{ ,,} \\ HNO_3 + NaOH &= 14689 \text{ ,,} \\ HNO_3 + KOH &= 14755 \text{ ,,} \end{aligned}$$

At room temperature these heats of neutralisation are about 1000 cal. smaller than at 0°.

The heat evolved on combustion, *i.e.* on the complete oxidation of combustible substances, is of particular interest. From the heat of combustion of an organic compound we can calculate its heat of formation. This quantity is of considerable importance, but cannot be measured directly, as the preparation of organic compounds from the elements is either impossible, or only possible under conditions which cannot be reproduced inside a calorimeter. It is necessary to emphasise the fact that only very rapid reactions can be treated calorimetrically, for the interchange of heat with the surroundings during a slow reaction becomes so great that even approximate measurements are impossible. As most organic reactions are very slow, we are forced to determine the heat of reaction by an indirect method, viz. from the determination of the heat of combustion.

The calculation of the heat of formation from the heat of combustion is as follows:

Let Q_1 be the heat of combustion of the hydrocarbon C_nH_{2n+2}; we have then

$$C_nH_{2n+2} + (3n+1)O = nCO_2 + (n+1)H_2O + Q_1. \quad \ldots\ldots(1)$$

For the formation of carbonic acid we have the equation

$$C + 2O = CO_2 + Q_2, \quad \ldots\ldots(2)$$

and for the formation of water,

$$H_2 + O = H_2O + Q_3. \quad \ldots\ldots(3)$$

* *Ann. d. Physik*, **18**, 755 (1905).

Multiplying (2) by n and (3) by $n+1$, and subtracting from (1), we obtain

$$C_nH_{2n+2} - nC - (n+1)H_2 = Q_1 - nQ_2 - (n+1)Q_3,$$

and hence for the formation of the hydrocarbon,

$$nC + (n+1)H_2 = C_nH_{2n+2} + nQ_2 + (n+1)Q_3 - Q_1.$$

For methan CH_4 we have $Q_1 = 213500$ cal., and since $Q_2 = 96000$ and $Q_3 = 58000$, the heat of formation

$$Q = 96000 + 2 \times 58000 - 213500 = 18500 \text{ cal.}$$

If the compound contain other elements, such as O, N, S, Cl, etc., the calculation is not altered in any essential particular. The calculation of the heat of formation is always possible when the products of combustion of the elements and their heats of formation are known.

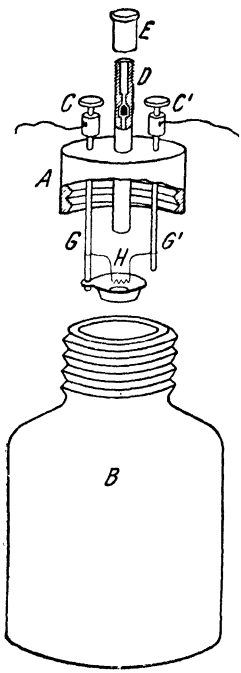


FIG. 16.

The most convenient apparatus for the experimental determination of the heat of combustion was devised by Berthelot, and has been used by him and by other investigators in the determination of the heats of combustion of a large number of substances. Berthelot's apparatus is shown in Fig. 16.

B is a strong steel cylinder furnished with a tightly fitting screw-cap A. Attached to this cap by the holder G is a capsule in which a portion of the organic substance is placed. Oxygen at a pressure of about 25 atmospheres is introduced through the valve D. E is a cap for the valve. Between G and G' is a fine iron wire, bent so as to be in contact with the substance in the capsule. After the cap has been screwed on and the cylinder has been charged with oxygen, the iron wire is heated by means of an electric current, led in through the terminals C and C'. In this way the substance is ignited and soon burns completely in the compressed oxygen.

The whole apparatus is contained in a water calorimeter, in which the rise in temperature produced by the combustion is measured. In calculating the heat of combustion, we must correct for the heat evolved in the combustion of the iron wire. The calorimeter may be calibrated with a substance of which we know the heat of combustion, or by reproducing with a known electric current the rise in temperature produced by the combustion. The heat of combustion is then equal to the electrical energy produced inside the cylinder.

The following table contains the heats of combustion of a number of important organic compounds:

Substance.	Formula.	Heat of combustion.	Heat of formation.
Methan	CH_4	213500	18500
Ethan	C_2H_6	372300	23300
Propan	C_3H_8	528400	30500
Butan	C_4H_{10}	687200	35000
Ethylene	C_2H_4	341100	−14600
Acetylene	C_2H_2	313800	−51400
Benzene	C_6H_6	784100	−4100
Toluene	C_7H_8	933800	2300
o-Xylol	C_8H_{10}	1084000	15200
Naphthalene	$C_{10}H_8$	1241800	−27400
Anthracene	$C_{14}H_{10}$	1694300	−33300
Methyl chloride	CH_3Cl	173700	29000
Methylene chloride	CH_2Cl_2	106800	31400
Chloroform	$CHCl_3$	89200	46600
Methyl bromide	CH_3B_2	180400	13600
Methyl iodide	CH_3I	194700	−3400
Methylene iodide	CH_2I_2	178400	−15100
Nitromethan	CH_3NO_2	169800	28800
Nitroethan	$C_2H_5NO_2$	322300	38800
Nitrobenzene	$C_6H_5NO_2$	—	5100
Trinitrobenzene 1, 3, 5	$C_6H_3(NO_2)_3$	663800	5500
Methyl alcohol	CH_3OH	170600	61400
Ethyl alcohol	C_2H_5OH	325700	69900
n-Propyl alcohol	C_3H_7OH	480300	78600
Methyl ether	$(CH_3)_2O$	344200	51500
Ethyl ether	$(C_2H_5)_2O$	651700	70500
Benzyl alcohol	C_7H_7OH	895300	38700
Glycol	$C_2H_4(OH)_2$	283300	113300
Glycerol	$C_3H_5(OH)_3$	397100	160900
Mannitol	$C_6H_8(OH)_6$	728500	320300

Substance.	Formula.	Heat of combustion.	Heat of formation.
Cane sugar	$C_{12}H_{22}O_{11}$	1355000	535600
Glucose	$C_6H_{12}O_6$	677200	302600
Phenol	C_6H_5OH	736000	36800
o-Nitrophenol	$C_6H_4(NO_2)OH$	688200	50100
Picric acid	$C_6H_2(NO_3)_3 . OH$	622500	46800
α-Naphthol	$C_{10}H_7OH$	1118500	30500
Formaldehyde	CH_2O	120800	25400
Acetaldehyde	C_2H_4O	279150	47450
Benzaldehyde	C_6H_5CHO	841700	23300
Acetone	C_3H_6O	426900	63000
Benzophenone	$C_6H_5COC_6H_5$	1558100	8900
Formic acid	CH_2O_2	61700	101500
Acetic acid	$C_2H_4O_2$	209400	117200
Propionic acid	$C_3H_6O_2$	367400	121600
Benzoic acid	$C_6H_5CO_2H$	772800	94200
Oxalic acid	$C_2H_2O_4$	60200	196800
Succinic acid	$C_4H_6O_4$	356800	226200
Tartaric acid	$C_4H_6O_6$	281000	302300
Urea	CON_2H_4	152200	79800

The heats of formation in the table are calculated for the states of matter (solid, liquid, or gaseous) to which the compound or elements in question belong at room temperature. The heats of combustion are given for constant pressure.*

For very accurate determinations E. Fischer and Wrede substitute a platinum resistance thermometer for the mercury thermometer, and emphasise the importance of efficient stirring of the water in the calorimeter. In this way they determined with the greatest care the heats of formation of cane sugar (3954 cal. per gram) and benzoic acid (6328 cal. per gram), and recommend these substances for the calibration of calorimeters.

In these determinations the weighings were corrected for the buoyancy of the air, and the heat equivalent of one watt-second was taken as 0·2390 cal.

Richards, Henderson, and Frevert, using the adiabatic method mentioned on a previous page, determined the heat of combustion of benzene and found it to be 2·5342 times as

* See Landolt-Börnstein, 3rd edition.

great as that of cane sugar. Using Fischer and Wrede's determination, we arrive at 10020 cal. for the heat of combustion of benzene.

The heat of combustion, and hence also the heat of formation of organic compounds depend in a marked degree upon their constitution, that is to say, they depend not only upon the number and nature of the atoms in the molecule, but also upon the manner in which they are bound together. Isomeric compounds may have totally different heats of formation. Thus acetone $CH_3 . CO . CH_3$ has a heat of combustion equal to 423000 cal., while the heat of combustion of its isomer allyl alcohol $CH_2 . CHCH_2(OH)$ is 465000 cal., and of its other isomer propionic aldehyde CH_3CH_2CHO is 441000 cal. Similarly, the heat of combustion of polymeric substances (per gram) varies with the size of the molecule, as the following table shows:

Acetylene C_2H_2 - -	12100	Acetaldehyde C_2H_4O -	6350
Benzene C_6H_6 - -	10000	Paraldehyde $(C_2H_4O)_3$ -	6160

A number of important regularities have been brought to light by the numerous researches of Thomsen, Berthelot, Stohmann, and others, which enable us to predict quantitatively the effect on the heat of combustion of a particular kind of bond between atoms or groups of atoms in the molecule.

Each of the groups CH_3, $C=H_2$, $C\equiv H$, CH_2OH, CHO, CO, etc., has a definite heat of combustion, its so-called thermo-chemical constant. We can calculate the heat of combustion of any compound by adding the thermo-chemical constants of all the groups in the molecule. Conversely, we can make important deductions from the heat of combustion as to the constitution of a compound. We can decide, for example, the existence of double or triple bonds in this way.

The calorimetric method of determining the constitution of a compound is, of course, less accurate the more complex the molecule, for the percentage effect on the heat of combustion of changes in the relative position of the molecules diminishes more and more as the complexity increases. This is most marked in the case of so-called desmotropic transformations, as these are generally accompanied by relatively small energy

changes. Yet the thermo-chemistry of these transformations would be of particular interest as affording a welcome confirmation of other methods of deciding the constitution, which are often exceedingly troublesome to carry out.

So far, however, sufficient material is not yet available for this purpose. Of late some very successful attempts have been made in this direction by Roth and Auwers and their colleagues.* They determined the heat of transformation by two methods whenever possible, viz. directly, by heating the substance electrically in a calorimeter, and, indirectly, by determining the heat of combustion of both forms.

As the heat of transformation is generally only a small fraction of the total heat of combustion, it is necessary to make the determinations with very great care.

Heat of reaction and temperature. Hitherto we have been regarding the heat of reaction as a constant quantity. On closer consideration, however, we are led to conclude that this cannot strictly be the case, but that the heat of reaction must vary with the temperature at which the reaction proceeds. Since the energy content of a substance or of a system of substances is a function of their temperature, it is clear that the difference in energy between two systems, which in chemical reactions is simply the heat of reaction, must also have a direct connection with the temperature.

The variation of the heat of reaction with the temperature was deduced by Kirchhoff in much the same way as we calculated the temperature coefficients of the heat of fusion and the heat of evaporation at the beginning of this paragraph. If we denote unit mass of the substances on the left-hand side of our chemical equation by I., and unit mass of the products of reaction on the right-hand side of the equation by II., we may go from system I., which we shall suppose to be at temperature T, to system II., at temperature $T+dT$, in two different ways. We may first let the reaction proceed at the constant temperature T and then raise the temperature of system II. by dT, or we may first raise the temperature

* Roth, *Zeit. f. Electrochem.* **16**, 654; **17**, 789 (1911). Auwers, Roth, u. Eisenlohr, *Ann. d. Chemie*, **373**, 234, 244, 267 (1910).

of system I. by dT and then allow the reaction to proceed at the constant temperature $T+dT$. As there is no work done in either case, the heat evolved in both cases must be the same. In the first case the heat evolved is $Q-c_2dT$, where c_2 is the sum of the specific heats (per mol.) of the substances formed (with evolution of heat) in the reaction. In the second case the heat evolved is $-c_1dT+Q+dQ$.

Hence $$Q+dQ-c_1dT=Q-c_2dT$$

or $$\frac{dQ}{dT}=c_1-c_2=-\Sigma c.$$

In the summation the specific heats of the substances which are produced with evolution of heat are reckoned positive. The temperature coefficient of the heat of reaction is therefore equal to the change in the heat capacity of the system, consequent on the reaction. The heat of reaction increases with temperature when the substances formed in the reaction have a smaller heat capacity than the substances which disappear; in the reverse case it decreases with temperature. For endothermic reactions in which Q is negative, an increase in Q means a diminution in the numerical value of the heat of reaction, and conversely.

The principle of Thomsen and Berthelot. On page 118 we drew attention to the fact that the heat of formation of a chemical compound is greater in general the more easily the compound is formed. Thus the alkali metals which oxidise spontaneously in air at the ordinary temperature have a greater heat of oxidation than carbon, for example, which does not begin to oxidise until it is heated. Carbon in turn unites more readily with oxygen than the heavy metals, which have a still smaller heat of oxidation. Conversely, compounds with a large heat of formation are difficult to split up into their constituents, while those with a small heat of formation are relatively easily decomposed. Thus the oxides of silver and mercury break up on heating alone, while the lighter metals can only be prepared from their oxides by means of strong reducing agents, or with the aid of the electric current. There can therefore be no doubt that there is some relation between chemical affinity and heat of reaction.

For this reason Jul. Thomsen (1851), and later Berthelot (1868), regarded the heat of reaction as a measure of the driving force of the reaction. Berthelot, in his *Essai de mécanique chimique*, enunciated the following "Principe du travail maximum" as the foundation of chemical dynamics. *Of all the possible chemical processes which can proceed without the aid of external energy, that process always takes place which is accompanied by the greatest evolution of heat.*

Berthelot's principle has proved to be at fault in the light of subsequent researches. Thus it is incapable of accounting for endothermic reactions. Although it is true at ordinary temperatures that most spontaneous reactions are accompanied by evolution of heat, yet at high temperatures there is a preponderance of reactions which involve an absorption of heat, as, for example, most dissociations, the formation of nitric oxide from nitrogen and oxygen, etc. Berthelot's principle, therefore, is merely a rule which generally holds good at low temperatures. It cannot nowadays be regarded as a strictly valid law.

In their endeavours to measure chemical forces by means of thermal quantities, Berthelot and Thomsen were undoubtedly guided by the law of the conservation of energy, but the principle of maximum work is by no means a necessary consequence of this law. The first law merely states that the (positive or negative) heat evolved in a chemical reaction is equal to the change in energy of the transformed substances. Under what conditions the reaction will take place or fail to take place is a question which it is beyond the scope of the first law of thermodynamics to decide. The direction in which an energy change will proceed can only be determined with the aid of the second law of thermodynamics.

CHAPTER V.

THE SECOND LAW OF THERMODYNAMICS.

1. Carnot's principle.

Reversible and irreversible processes. In discussing Berthelot's principle we were led to ask the question whether or not it is possible to deduce the direction of a chemical reaction from the magnitude or the sign of the heat evolution which accompanies it. In other words: If a quantity of heat $+Q$ is set free in going from a state A to a state B, will the change always take place from A to B, or, if not, under what conditions will it do so? Or in general: Under what conditions can we predict the direction in which any particular process will go?

The first law of thermodynamics fails to give us the information we desire. We may define the limits of the first law as follows: If any change of state takes place in an isolated system, the total energy remains constant, but the law of the conservation of energy tells us nothing as to the conditions which determine whether the change of state will take place or not. On the other hand, it is the object of science not only to determine the changes which would be produced by a hypothetical process, but also to predict the circumstances under which the process will take place. To quote a saying of Ostwald's, "Science is the very art of prophecy" (Die Wissenschaft ist geradezu die Kunst des Prophezeiens).

We are therefore always trying to find new laws by means of which we may predict the occurrence of natural phenomena and the course which they will take. In the following we shall become acquainted with a law which, like the law of the

conservation of energy, is applicable to all processes in which energy is transformed, and which enables us to predict the course which subsequent transformations will take, if we know the initial state of the system. This law is known as the second law of thermodynamics.

In order to arrive at a statement of this law, let us consider a few simple changes of state which we are able to predict with absolute certainty from the initial conditions of the system. When two bodies of unequal temperature are brought into contact, heat will flow from the hotter body to the colder until the temperature is the same in both bodies. If the two bodies are not in actual contact, heat will be interchanged by radiation until the temperatures have been equalised. A body at uniform temperature in all its parts will never of its own accord become hot at one part and cool at another. The interchange of heat by conduction or by radiation is therefore an *irreversible* process. This empirical fact is the kernel of the second law. Although it is a direct consequence of our every-day experience, this law was first recognised in its full importance by Sadi Carnot, an engineer officer in the French army, who died of cholera in 1832. Its subsequent development is largely due to R. Clausius. Carnot's principle may be stated as follows: Heat can never go from a hotter body to a colder body without compensation, *i.e.* without the production of a permanent change in the surroundings.

Besides the transfer of heat from places of higher to places of lower temperature, there are a number of other simple irreversible processes. The most important are:

The production of heat by friction.

The expansion of a gas into a vacuum.

The diffusion of gases or liquids.

The production of heat by the electric current.

The spontaneous production of heat in chemical reactions.

All these irreversible processes take place spontaneously whenever occasion offers. A gas always flows into a vacuum when there is no obstruction to its flow. The electric current always produces heat in flowing through a resistance, and so on.

If we could construct a machine which, after operating, would leave all its parts in their original condition, and which would

merely convert a quantity of heat into the equivalent amount of work, we should have a means of reversing without compensation any of the processes which we have just said were irreversible.

This is at once apparent for the production of heat by friction. The transfer of heat from a body of higher to a body of lower temperature could be reversed by withdrawing heat from the cold body and converting it into work, and then using the work obtained to heat the hotter body by friction, and thus raise its temperature to the initial value. The expansion of a gas into a vacuum could be reversed by first doing work in compressing the gas, and then reconverting the heat produced into the amount of work used in the compression. All the other processes which we enumerated above as typically irreversible could be reversed by means of this hypothetical machine. We are therefore not justified in stating that these processes are irreversible until we have shown that our hypothetical machine is not consistent with experience. The second law is thus equivalent to the statement that *the conversion of heat into work is never the sole result of a natural process.* In any actual process by which heat is converted into work we always find that some other changes have been produced at the same time. For example, when a gas becomes cooler by doing work in expanding, its volume is changed simultaneously. [Chemical changes are produced by the explosion of the gases in the cylinder of a gas engine, and here, as in the steam engine, only part of the heat evolved is converted into work while part is absorbed by the cooling water.] The conversion of heat into work is thus invariably accompanied by an irreversible process.

To illustrate the scope of this statement, let us return for a moment to our hypothetical machine. Since the operation of the machine produces no permanent change in the bodies of which it is composed, it must go through what is called a cyclical process, *i.e.* one in which the machine returns to its original state, and which may therefore be repeated as often as we please.

In other words, our machine runs periodically. The realisation of a machine of this kind would enable us to withdraw

all the heat from a large heat reservoir and convert it into useful work. A ship furnished with an engine of this kind could make use of the enormous quantities of heat stored in the ocean, and could thus be driven for an almost indefinite time without fuel of any kind. An engine of this kind is not inconsistent with the first law. A ship driven by such an engine would not run for ever, since the work done is not created from nothing, but is obtained from the heat stored up in the sea. We should, however, be able to obtain enormous amounts of work in this way. The operation of a machine of this kind has been called by Ostwald "perpetual motion of the second kind." According to Ostwald, the second law is the statement that the realisation of perpetual motion of the second kind is impossible.

The second law as well as the law of the conservation of energy are both empirical laws, but they have a much higher degree of certainty for us than most other laws derived from experiment. The conviction of the validity of the second law, which dominates all scientific thought at the present time, is not based merely on the fact that no one has yet succeeded in constructing a machine which would convert the heat store of the ocean into useful work. The irreversible processes which have been observed daily for hundreds of years constitute the most convincing evidence in favour of the second law. We shall not doubt its validity until we find a body of uniform temperature separating of itself into a hotter and a colder portion, or until we see a gas contracting of its own accord and leaving a vacuum behind. In addition we find that the deductions which have been made from the second law of late years in chemistry and physics are all confirmed by experiment.

Although the existence of irreversible processes in nature is now an established fact, the question as to the possibility of a completely reversible process must still remain open. A process is said to be reversible when it can be carried out in either direction, and when the intermediate states of the system are the same in both directions, but follow one another in the reverse order. The result of two opposite reversible processes must be nil, not only with regard to the system which we are considering, but also with regard to its surroundings. A process

is said to be irreversible even when only a small part of it is not reversible. The oscillation of a mathematical pendulum is an example of an ideal reversible process. All processes considered in pure dynamics are also completely reversible. All actual mechanical processes, on the other hand, are irreversible, as they are always accompanied by friction, and consequently by irreversible production of heat. Any actual pendulum comes to rest after a certain number of oscillations unless it is kept in motion—as in a clock—by means of a spring, or weight and pulley, that is to say, by the expenditure of external work. The less the pendulum is retarded by friction, the more nearly the oscillation approximates to a completely reversible process. Although we can never realise a completely reversible process in practice, we can attain more and more nearly to it by refining our apparatus. The consideration of strictly reversible processes, as in pure dynamics for example, has proved to be of very great importance in the progress of science. The conception of perfectly reversible processes is also of great use in thermodynamics, as we shall show in the following.

The change in volume of a gas again illustrates the difference between reversible and irreversible processes. The adiabatic compression of a gas (see p. 91) is reversible, as the initial state may be re-established completely by an adiabatic expansion. In practice, however, it is impossible to construct vessels absolutely impermeable to heat. No actual compression is therefore strictly adiabatic, as some of the heat produced is always lost by conduction or radiation to the surroundings. The less the permeability of the walls of the vessel, the smaller this loss in heat will be, and the more nearly will the change in volume approximate to a reversible process.

Similar considerations apply to reversible isothermal changes of volume. These also can only be realised approximately. An isothermal compression or dilatation cannot be completely reversible, unless the pressure which causes the piston to move differs only by an infinitesimal quantity from the pressure in the interior of the gas, for in this case only is the driving force, and hence the velocity of the change, infinitesimally small. If the piston were to move rapidly, we should have in the first

instance a loss of heat by friction, and, secondly, the heat evolved in the compression (or dilatation) would not be given up to the surroundings with sufficient rapidity, so that the temperature would not remain strictly constant.

Further examples of reversible processes will be dealt with in subsequent chapters. In most cases we may imagine complete reversibility to be attained by carrying out the process sufficiently slowly, so that the driving force would be infinitely small and the system would always be in a state of equilibrium. All strictly reversible processes must therefore go through a continuous series of states of equilibrium. From this condition alone it follows that all spontaneous processes in Nature, which lead from unstable states to states of equilibrium, must be irreversible.

By the second law of thermodynamics it follows that every transformation of heat into work must be accompanied by irreversible processes. We shall now investigate these transformations more closely, and shall begin with an exact analysis of the processes which take place in heat engines. We shall take the steam engine as the simplest and, historically, the most important example.

By supplying heat to the boiler we convert the water into steam, which does work in pushing the piston forward. In the return stroke, when the steam is condensed to water, part of the heat supplied to the boiler is given up at a lower temperature to the surroundings (condenser). The condensed water is then returned to the boiler, and has thus completed a cyclical process.

The transformation of heat into work is not the only process which takes place in the steam engine, as it would be in a perpetual motion machine of the second kind. A certain quantity of heat has also been removed from the boiler at a high temperature and given up at a lower temperature to the condenser. In practice we find, therefore, that a machine working periodically can convert heat into work if at the same time it takes a certain quantity of heat from a source at a high temperature and gives it up again to a sink at a lower temperature.

Carnot's cycle. The question now arises, what is the ratio

of the heat converted into work to the total heat taken from the source at the temperature T_1 in a cycle of this kind, which we may suppose to operate between the temperatures T_1 and T_2 ($T_1 > T_2$)?

In the first instance we see that the efficiency is greater the fewer the irreversible processes involved in the cycle, for we have shown that these can only be reversed by the expenditure of additional work or heat (*e.g.* by the consumption of additional fuel). A machine in which the loss by friction or by radiation or conduction of heat is excluded, that is to say, a machine which makes use only of reversible processes (see p. 88), will therefore have maximum efficiency. Although it is impossible in practice to exclude completely such losses of energy, we may regard the maximum efficiency of a reversible engine as an upper limit, which may be approached more or less nearly according to the skill of the engineer, but which can never be exceeded. The maximum efficiency is a quantity which is characteristic of each type of machine.

We can prove by the second law that all periodic machines working reversibly between the temperatures T_1 and T_2 convert the same fraction of the heat Q_1 absorbed at the temperature T_1 into work, and give up the same remainder Q_2 to the surroundings at the lower temperature T_2. In other words, for a given amount of heat absorbed Q_1 the maximum amount of work $Q_1 - Q_2$, which can be produced, is dependent only on the temperatures T_1 and T_2 of source and sink, and does not depend on the nature of the machine or on the chemical nature of the working substance (*e.g.* water, alcohol, etc.).

If this were not the case, if, for example, it were possible for a reversible machine I. working between T_1 and T_2 to convert a greater fraction w of the heat Q_1 into work than another reversible machine II. working between the same temperatures and producing only the amount of work $w' < w$, it would be possible to combine these two machines by making I. drive II. in the reverse direction, so that II. would not convert heat into work, but work into heat. By our hypothesis I. will then give up the quantity of heat $Q_2 = Q_1 - w$ to the surroundings at the lower temperature T_2, and II. will absorb the larger amount

$Q_2' = Q_2 - w'$ from the surroundings, so that the compound engine will absorb $Q_2' - Q_2$ from the surroundings at the temperature T_2. Engine I. will absorb Q_1 and engine II. will give up Q_1 to the source at the higher temperature T_1, so that its heat content will remain unaltered. The work done by the compound engine is $w - w' = Q_1 - Q_2 - (Q_1 - Q_2') = Q_2' - Q_2$. In all, therefore, the compound engine would absorb $Q_2' - Q_2$ from the sink at temperature T_2 and convert it completely into work. As this process could be repeated periodically as often as we pleased, the compound engine I.+II. would be a perpetual motion machine of the second kind, and therefore inconsistent with the second law.

Hence all periodic reversible heat engines working between the same two temperatures must convert the same fraction of the heat absorbed at the higher temperature into work. The maximum efficiency of a heat engine therefore depends only on the temperatures between which it works. In order to calculate this function of the temperature it is sufficient to determine the work done in an arbitrary reversible cycle, which we may perform with any arbitrarily chosen working substance. For simplicity we shall choose a perfect gas as working substance, as its equation of condition is accurately known. The reversible cycle which we shall suppose it to perform is known as Carnot's cycle. It is as follows :

1. Consider a molecule of a perfect gas of volume v_1, absolute temperature T_1, and pressure p_1, enclosed in a cylinder with a frictionless piston and immersed in a large heat reservoir at the same temperature T_1. If we reduce the pressure on the piston, the gas will expand and do work in pushing the piston forward. The work done during the small increase in volume dv is $p\,dv$, if p is the pressure which has to be overcome in the expansion (see p. 88). The work done in expanding to the volume v_2 is therefore

$$w_1 = \int_{v_1}^{v_2} p\,dv.$$

This quantity is greater, the greater the pressure p which has to be overcome in the expansion. It will attain to its greatest value when the external pressure is equal to, or only infinitesi-

mally different from, the pressure in the interior of the gas. To calculate the maximum amount of work which can be obtained from the expansion, we must therefore substitute for p the pressure in the interior of the gas. By the equation of condition $pv = RT$, we have

$$w_1 = \int_{v_1}^{v_2} \frac{RT}{v}\, dv.$$

As the gas is immersed in a large heat reservoir at temperature T_1 its temperature remains constant during the expansion. Hence, by integration,

$$w_1 = RT_1 ln \frac{v_2}{v_1}.$$

By the first law the heat Q_1 absorbed by the gas during the expansion must be equal to the work done. Hence

$$Q_1 = w_1 = RT_1 ln \frac{v_2}{v_1}.$$

2. (Adiabatic expansion.) Let the cylinder be removed from the heat reservoir and surrounded by a layer of perfectly non-conducting material. By gradually diminishing the pressure on the piston, let the gas expand further until its volume is v_3. As interchange of heat is prevented by the non-conducting layer, the molecules of the gas must lose kinetic energy as they do work in pushing back the piston. Hence their mean kinetic energy must diminish, and the temperature will fall to T_2. The work done w_2 must be equal to the diminution in the kinetic (heat) energy of the gas.

3. Let the gas now be removed to a heat reservoir of temperature T_2, and compressed reversibly and isothermally, as in 1, until its volume is $v_4 < v_3$, but $> v_1$. The work done on the gas is $w_3 = RT_2 ln \frac{v_3}{v_4}$, and an equal quantity of heat $Q_2 = w_3$ is given out to the reservoir.

4. Finally, let the gas be surrounded by a non-conducting layer, as in 2, and compressed adiabatically until its temperature has returned to its initial value T_1. We shall suppose the volume v_4 to have been chosen so that the subsequent adiabatic compression would just bring the volume back to its initial

value v_1, thus completing the cycle. In the adiabatic compression 4, let the work done on the gas be w_4.

Fig. 17 is a graphical representation of Carnot's cycle. The isothermals are horizontal lines, and the adiabatics are curves convex to the v-axis. By the first law the heat absorbed from the surroundings in the cycle must be equal to the work done, so that

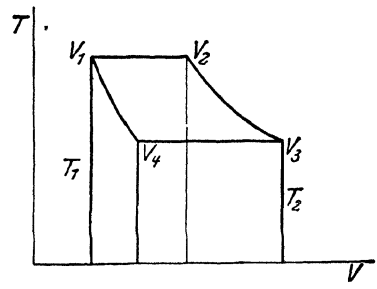


FIG. 17.

$$Q_1 - Q_2 = w_1 + w_2 - w_3 - w_4.$$

The heat energy produced by the adiabatic compression 4, which raised the temperature of the gas from T_2 to T_1, is $w_4 = c_v(T_1 - T_2)$, where c_v is the specific heat of the gas (at constant volume) which is independent of the volume. The heat energy converted into work in the adiabatic expansion 3 has the same value.

Hence $$w_2 - w_4 = 0$$

and $$Q_1 - Q_2 = w_1 - w_3 = RT_1 ln \frac{v_2}{v_1} - RT_2 ln \frac{v_3}{v_4}.$$

The volume v_3 was produced by adiabatic expansion from v_2 and v_1 by adiabatic compression from v_4. Hence, by p. 91,

$$\frac{v_3}{v_2} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{k-1}} \text{ and } \frac{v_4}{v_1} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{k-1}},$$

and hence $$\frac{v_3}{v_2} = \frac{v_4}{v_1} \text{ and } \frac{v_1}{v_2} = \frac{v_4}{v_3}.$$

Thus $$Q_1 - Q_2 = R(T_1 - T_2) ln \frac{v_2}{v_1}.$$

To calculate the efficiency of the cycle, we must divide the work done $Q_1 - Q_2$ by the total heat absorbed by the gas Q_1, and obtain

$$\frac{Q_1 - Q_2}{Q_1} = \frac{R(T_1 - T_2) ln \frac{v_2}{v_1}}{RT_1 ln \frac{v_2}{v_1}} = \frac{T_1 - T_2}{T_1}. \quad \ldots\ldots\ldots\ldots (1)$$

We thus obtain the strikingly simple result that the efficiency of Carnot's cycle, and hence, for the reasons above stated, the maximum efficiency of every other periodic machine, is directly proportional to the difference between the temperatures of the source and sink, and inversely proportional to the temperature of the source.

In many text-books and treatises, temperature and pressure, or pressure and volume, are chosen instead of volume and temperature as axes of coordinates in the graphic representation of such changes of state. Theoretically, any of these

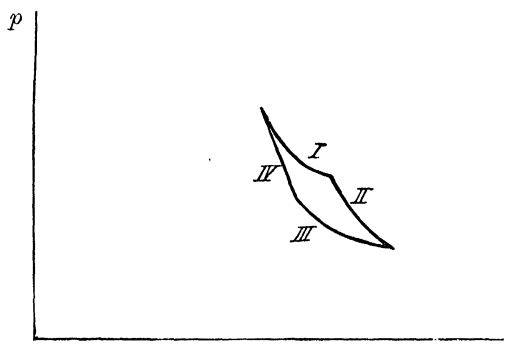


FIG. 18.

methods is equally justifiable, as the state of a system is completely determined (by a point in the diagram) when any two of the variables are given. The method chosen above (v and T as coordinates) has the advantage that the isothermals are all horizontal straight lines. If we choose p and v as coordinates, the area enclosed by the diagram is equal to the work done in the cycle, for it is equal to $\int p\,dv$ taken over the closed curve. Carnot's cycle in the pv diagram is shown in Fig. 18. The isothermals I. and III. are rectangular hyperbolas.

2. The concept of entropy.

By a simple transformation we obtain equation (1) in the form

$$\frac{Q_1}{T_1}-\frac{Q_2}{T_2}=0. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1a)$$

Here $+Q$ is the heat *absorbed* at temperature T_1 and $-Q$ the heat *given out* at temperature T_2. From now onwards we shall regard heat absorbed by the system as positive and heat given out as negative, so that $+Q_2<0$ and equation (1*a*) becomes

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}=0. \quad \text{.....(1}b\text{)}$$

The sum of the quantities of heat absorbed in the reversible cycle, each divided by the absolute temperature at which the absorption took place, is zero.

If portions of the cycle are irreversible, if, for example, part of the heat absorbed at T_1 reaches T_2 by radiation or conduction, the efficiency will be less than that of the reversible cycle. Thus, using the new convention as to the sign of Q, we have

$$\frac{Q_1+Q_2}{Q_1}<\frac{T_1-T_2}{T_1} \quad \text{.....(2)}$$

or

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}<0. \quad \text{.....(2}a\text{)}$$

A cycle in which the (positive or negative) heat absorption takes place at two temperatures only was called by Clausius (*Mechanische Wärmetheorie*, vol. i. p. 87) a simple cycle. We shall now prove that any cycle may be regarded as a sum of simple cycles.

Any reversible change of state leading from the state A to a different state B, represented by the points A and B in the v_1T diagram (Fig. 19), may be replaced by a series of adiabatic and isothermal changes. Thus we should have approximately the same change of state if we substituted a broken line composed of adiabatics and isothermals for the smooth curve AB. The smaller we make the little adiabatic and isothermal portions of our broken line, the closer will it approach to the actual curve AB. We can thus resolve any change of state from A to B

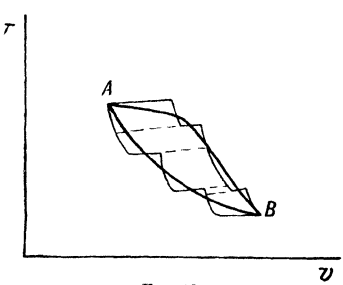


FIG. 19.

into a sequence of infinitely small adiabatic and isothermal changes.

If we close the cycle by returning from A to B along any other curve, we may resolve this return curve also into a similar series of isothermals and adiabatics.

Now let all these adiabatics and isothermals be produced until they cut the neighbouring isothermals and adiabatics, as in the figure. In this way we have divided the surface of the diagram into a number of quadrilateral figures each bounded by an isothermal and an adiabatic. Each of these quadrilaterals represents a simple reversible cycle, to which the equation

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}=0$$

is applicable. For the whole cycle represented by the broken line ABA, we have the equation

$$\Sigma\frac{Q}{T}=0,$$

where the summation is to be carried out over all the simple cycles. The summation $\Sigma\frac{Q}{T}$ need only be carried out for the boundary curve, as each of the lines in the interior of the diagram is described once in either direction, so that the part which they contribute to the sum must vanish. The equation

$$\Sigma\frac{Q}{T}=0$$

will hold more accurately for the smooth curve, the shorter we make the individual adiabatics and isothermals. Hence the equation

$$\int\frac{dQ}{T}=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

will hold strictly for the reversible cycle ABA. This relation must be valid for every reversible cycle through A and B, so that we may return from B to A by any path we choose, provided it be reversible. We can resolve $\int\frac{dQ}{T}$ taken round the cycle into the two integrals,

$$\int_A^B\frac{dQ}{T}+\int_B^A\frac{dQ}{T},$$

which are both independent of the path by which we go from A to B or from B to A. It is therefore clear that the value of the expression $\int_A^B \frac{dQ}{T}$ must depend solely on the initial state A and the final state B. It is therefore equal to the change of a single-valued function S of the variables v and T,

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

or

$$dS = \frac{dQ}{T}.$$

The function S, which, like the energy U, has a characteristic value for each state of the system, is called the entropy of the system. (This term was invented by Clausius, and is derived from the Greek word ἐντρόπειν, to change.) The entropy is defined by the above equations. The change in entropy is equal to the sum of all the quantities of heat which the system has been made to absorb reversibly and isothermally, each divided by the temperature at which the absorption of heat took place.

From the definition of entropy $S = \int dS = \int \frac{dQ}{T} + \text{const.}$, it follows that the entropy of any system, like its energy, contains a constant which is not determined by thermodynamics. It follows further that the entropy of a composite system, like its energy, is equal to the sum of the entropies of the component systems, since the value of the integral is independent of the path by which the system reaches its final state. It is therefore the same whether we take the system as a whole from an arbitrary initial state to the final state, or whether we take each of the components separately from the initial to the final state and then recombine them to form the system in its final state. The entropy of a system made up of the component systems 1, 2, 3, ... is therefore

$$S = S_1 + S_2 + S_3 + \dots .$$

From the equation $dS = \frac{dQ}{T}$ it follows further that the entropy of a body is not affected by an adiabatic change ($dQ = 0$). For

this reason Clausius also used the term "isentropic" for adiabatic change of state.

We can calculate the entropy S of a system of substances as a function of the variables of condition, just as we can calculate its energy U, provided we know the equation of condition.

For a molecule of an ideal gas, we have (see (2), p. 86)

$$dS = \frac{dQ}{T} = \frac{c_v dT + p\,dv}{T} = c_v \frac{dT}{T} + \frac{R\,dv}{v}.$$

If c_v is independent of the temperature, we have

$$S = c_v \int \frac{dT}{T} + R \int \frac{dv}{v} + \text{const.}$$

$$= c_v ln T + R ln v + S'.$$

We can thus determine the entropy of a perfect gas, apart from the arbitrary constant S', as a function of the temperature T and the molecular volume v. The constant S' is the entropy of the gas at the temperature $T = 1$ and the volume $v = 1$. Its numerical value is therefore dependent on the units in which we measure temperature and volume. For a given system of units S' has a definite value, like the molecular weight, for each gas. It is therefore a constant characteristic of the substance, and cannot be calculated by thermodynamics.*

The change in entropy in an isothermal compression from v_1 to $v_2 (v_1 > v_2)$ is therefore

$$S_{v_1} - S_{v_2} = R ln \frac{v_1}{v_2}.$$

The entropy is diminished by isothermal compression and increased by isothermal expansion.

Irreversible processes. We shall consider here only changes which occur in isolated systems. When we say that a system is isolated, we mean that all changes occurring in the system are independent of all changes occurring elsewhere. Thus an isolated system can neither do work nor absorb heat, since the work

* We see from the derivation of the law of mass action, given in chap. viii., that the constant S' cannot be chosen arbitrarily. If S' were entirely arbitrary, a chemical equilibrium would also be indeterminate, and this, as we shall show later, would be contrary to experience and to the second law.

done or the heat absorbed would produce changes in the surroundings dependent on changes in the system. The restriction to isolated systems involves no loss in generality, since we may consider a change in any system whatever as occurring in the isolated system composed of the system and its surroundings.

A very general way of stating the second law is the following:

An isolated system which has changed spontaneously from one state to another cannot be brought back to its original state without the expenditure of work.

If this were not so, we could obtain perpetual change at no expense of work by constant repetition of the process, thus violating the second law.

Since any method of undoing the spontaneous change of state involves expenditure of work, a reversible method of undoing it will also require expenditure of work, and hence the direct change if carried out reversibly must yield work. Hence, if an isolated system can change spontaneously from one state to another, work can be gained by causing the same change in the state of the system to take place in a reversible manner.

Let us consider a spontaneous irreversible change from state A to state B in an isolated system and the corresponding reversible change by which the system can be made to undergo the same change of state.

During the reversible change the system cannot be isolated, since it does work on the surroundings. The reversible change may, however, be isodynamic (*i.e.* not involving a change in the energy of the system), since the energy of the system in state A is equal to its energy in state B. However the reversible change is carried out, it must involve the absorption by the system of an amount of heat equivalent to the work done by the system, for this is the only way in which a system can do work without a change in energy. A reversible change in a system which is accompanied by an absorption of heat must by definition be accompanied by an increase in the entropy of the system. Hence the entropy of the system in state B must be greater than in state A.

As a simple example of a spontaneous irreversible process let us take the flow of a gas into a vacuum, as in the Gay-Lussac

experiment (p. 86). A mol of the gas originally at pressure p, in a vessel of volume v_1, is allowed to flow through a stopcock into an evacuated vessel of volume v'. Both vessels are immersed in a calorimeter at temperature T. Except for the slight Joule-Thomson effect, which is zero for a perfect gas, the temperature is not altered in the process. The walls of both vessels may therefore be made of non-conducting material, so that the region bounded by the walls of the two vessels may be regarded as an isolated system. No work is done by the system and no heat is absorbed in the process. When equilibrium is reached, the gas is distributed uniformly throughout both vessels at the pressure $p\frac{v_1}{v_1+v'}=p_1\frac{v_1}{v_2}$, where v_2 is the total volume finally occupied by the gas. The same change in the state of the gas may be brought about reversibly by allowing the gas to expand isothermally and do work against a piston. The work done in this case is

$$w=p\,dv=RTln\frac{v_2}{v_1},$$

and the heat absorbed is equal to this, *i.e.*

$$Q=RTln\frac{v_2}{v_1}.$$

The increase in entropy is therefore

$$\Delta S=\frac{Q}{T}=Rln\frac{v_2}{v_1},$$

a result which we obtained on p. 143 by a slightly different method.

The spontaneous diffusion of one gas into another may be treated in a similar manner. The result of the diffusion is the uniform distribution of both gases through the whole volume originally occupied by the gases separately. The two gases (if perfect) form an isolated system, since no work is done and no heat is absorbed in the process. The same change in the state of the system may be brought about reversibly by means of two membranes each permeable to only one of the gases. Initially both membranes are placed at the boundary between the two gases and each is furnished with a piston rod. Each membrane is then forced by the partial pressure of the gas to which it is

impermeable, through the gas to which it is permeable until both gases are distributed uniformly throughout the whole volume. If we have a mol of each gas, the heat absorbed which is equal to the work done in the process is

$$Q = RTln\frac{v_1+v_2}{v_1} + RTln\frac{v_1+v_2}{v_2}$$
$$= 2RTln(v_1+v_2) - RTlnv_1 - RTlnv_2.$$

The increase in entropy is therefore

$$\Delta S = \frac{Q}{T} = 2Rln(v_1+v_2) - Rlnv_1 - Rlnv_2.$$

On p. 143 we showed that the entropy of the gases (before diffusion) are respectively

$$S = c_v lnT + Rlnv_1 + S_1,$$
$$S' = c_v' lnT + Rlnv_2 + S_1'.$$

The entropy of the whole system after diffusion has taken place is therefore

$$S + S' + \Delta S = (c_v + c_v')lnT + 2Rln(v_1+v_2) + S_1 + S_1'.$$

This is the greatest value which the entropy can assume under the given conditions.

We may now state the second law of thermodynamics in the following form.

All natural spontaneous changes in an isolated system involve an increase in its entropy.

Conversely, we conclude that an isolated system will not undergo a spontaneous change, *i.e.* will be in equilibrium, if all possible changes which are consistent with the character of the system leave the entropy unaltered, or cause it to diminish. In other words, the system is in equilibrium when its entropy is a maximum.

There is an analogous theorem to this in pure dynamics, viz. a mechanical system is in equilibrium when its potential energy is a minimum.

The following consideration of Planck (8 *Vorlesungen über theoretische Physik*, 1910, p. 16) will facilitate the conception of entropy, and thus help us to understand the second law. Let a spontaneous natural process in an isolated system lead

from state A to state B. We know by experience that it is impossible to reverse the process $A \rightarrow B$ completely and return to the state A. State A must therefore differ from state B in some way. We might almost say that nature appeared to have a greater preference for state B than for state A, or that a natural process is only possible when nature has a greater preference for the final than for the initial state.

Our object must now be to find some physical quantity which we may take as a measure of this preference of nature. This quantity must, like the energy for example, be a function of the state alone, and not of the past history of the system before it reached this state.

This quantity would have the property of becoming greater in all irreversible changes and remaining constant in all reversible changes. In entropy we have become acquainted with a quantity which complies with these conditions, and which may therefore be taken as a measure of the preference of nature for a state.

We may now summarise the two laws of thermodynamics as follows:

First law: All possible changes of state in an isolated system leave its energy unaltered.

Second law: All possible (spontaneous) changes of state in an isolated system produce an increase in its entropy.

We must emphasise the fact that the second law was deduced without the aid of any hypothesis from the experimental observation that heat never goes of its own accord from places of lower to places of higher temperature. The analytical form in which the second law was stated in equations (2) and (3) was, no doubt, deduced from the gas laws, which do not apply rigidly to any real gas. We might conclude from this that the equations (2) and (3), like the gas laws, are only valid approximately. This conclusion would, however, be erroneous. The essence of the second law is the statement that the efficiency of a cycle between any two temperatures must be independent of the working substance. We may therefore imagine the cycle to be performed with a hypothetical gas having the properties defined by the equation $pv = RT$.

This mental experiment would not invalidate our deductions any more than the assumption of perfectly reversible processes, which also is only justifiable in the limiting case. Lord Kelvin avoids the use of the ideal gas altogether by defining the absolute scale of temperature in terms of the second law.

The second law tells us that in a reversible cycle performed between the temperatures t and $t-dt$ measured on any arbitrary scale, the ratio of the heat converted into work to the total heat absorbed at temperature t is a function of the temperatures t and $t-dt$ alone, *i.e.*

$$\frac{dQ}{Q}=f(t, t-dt).$$

We may now define our scale of temperature θ so that equal degrees on the scale correspond to equal efficiencies, so that

$$\frac{dQ}{Q}=d\theta \quad \text{or} \quad ln\frac{Q_1}{Q_2}=\theta_1-\theta_2.$$

Two temperatures differ by 1° on the thermodynamic scale when a cycle performed between the temperatures has the efficiency

$$\frac{Q_1-Q_2}{Q_1}=1-\frac{1}{e}=1-0{\cdot}368=0{\cdot}632.$$

The relation between this thermodynamic temperature θ and the absolute gas temperature T is thus

$$d\theta=\frac{dT}{T} \quad \text{or} \quad \theta=lnT+\text{const.}$$

This definition determines the size of a degree, but leaves the zero point on the scale indeterminate.

In order to define the thermodynamic scale uniquely, we must determine the numerical value of the additive constant. Taking the constant as zero, we have coincidence with the ordinary temperature scale. Thus the freezing point of water ($T=273°$ absolute) becomes $ln273$ on the thermodynamic scale, and we have $\theta=lnT$ or $T=e^{\theta}$. It follows from the equation $\theta=lnT$ that θ becomes equal to $-\infty$ at the absolute zero ($T=0$). This harmonises with the fact that we are unable in practice

to reach the absolute zero, and can only approach it with very great difficulty.

The simplicity of the relationship between the thermodynamic scale and the gas thermometer scale is due principally to the simple properties of rarefied gases, and also to the fortunate choice of mercury as thermometric substance by Celsius and Reaumur before the discovery of the gas laws. The coefficient of expansion of mercury happens to be almost exactly proportional to the coefficient of expansion of rarefied gases. All our thermodynamical relationships would have been very much more complicated had water or alcohol, for example, or the resistance of a metal, been used for the definition of the practical scale of temperature. Their strict validity, however, would not have been affected.

At the beginning of this chapter (p. 129) we put the question: "Under what conditions can we predict the direction in which any particular process will go?" In answer we may now say: "The process will take place in the direction which involves an increase in the entropy of the system." It must therefore be one of the objects of science to determine the entropy of any given system as a function of its variables of condition. On p. 143 we have shown how this may be done for a perfect gas. In other cases the problem is not so simple, but the calculation is always possible if we know the equation of condition, *e.g.* van der Waals' equation for real gases. Yet even when it is not possible to obtain an explicit expression for the entropy, the entropy law can lead us to important conclusions, just as the law of the conservation of energy is important in many cases in which we are unable to give a numerical or analytical value for the energy of the system.

3. Consequences of the first and second laws.

Thermodynamic equations. For any change of state we have, by the first law,

$$dU = dQ - dw = dQ - p\,dv. \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

For reversible processes we have, by the second law,

$$\frac{dQ}{T} = dS. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

dU and dS are both complete differentials, so that we may write

$$dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and

$$dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial v} dv. \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Substituting (2), (3) and (4) in (1), we obtain

$$\frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv = T \frac{\partial S}{\partial T} dT + \left(T \frac{\partial S}{\partial v} - p \right) dv.$$

As this equation is true for all values of dT and dv, the coefficients of dT and dv must be equal to one another respectively.

Hence

$$\frac{\partial U}{\partial T} = T \frac{\partial S}{\partial T} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

and

$$\frac{\partial U}{\partial v} = T \frac{\partial S}{\partial v} - p. \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

We can eliminate the differential coefficients of the entropy from (5) and (6). Solving (5) for $\frac{\partial S}{\partial T}$ and (6) for $\frac{\partial S}{\partial v}$, and differentiating (5) partially with respect to v and (6) with respect to T, we obtain

$$\frac{\partial^2 S}{\partial T \partial v} = \frac{1}{T} \frac{\partial^2 U}{\partial T \partial v} = \frac{\frac{\partial^2 U}{\partial v \partial T} + \frac{\partial p}{\partial T}}{T} - \frac{\frac{\partial U}{\partial v} + p}{T^2},$$

and hence

$$\frac{\partial U}{\partial v} + p = T \frac{\partial p}{\partial T}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The expression on the left-hand side of this equation is a measure of the difference of the specific heats $c_p - c_v$, for it follows from the equation,

$$dQ = dU + p\,dv = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv + p\,dv,$$

that

$$c_p = \frac{\partial U}{\partial T} + \left(\frac{\partial U}{\partial v} + p \right) \frac{\partial v}{\partial T}$$

and

$$c_v = \frac{\partial U}{\partial T},$$

and hence, by (7),

$$c_p - c_v = \left(\frac{\partial U}{\partial v} + p \right) \frac{dv}{\partial T} = T \frac{\partial p}{\partial T} \frac{\partial v}{\partial T}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$\frac{\partial v}{\partial T}$ is the coefficient of expansion at constant pressure, and $\frac{\partial p}{\partial T}$ is the temperature coefficient of the pressure at constant volume. Both of these can be determined experimentally, although the determination of $\frac{\partial p}{\partial T}$ is troublesome for solids and liquids. It is easier in practice to measure the compressibility $\frac{\partial v}{\partial p}$, which we shall therefore substitute for $\frac{\partial p}{\partial T}$ in (8).

As v is a function of p and T, say $v=f(p, T)$, we have, by the rules of the differential calculus,

$$\frac{\partial p}{\partial T} = -\frac{\frac{\partial v}{\partial T}}{\frac{\partial v}{\partial p}}.$$

Hence equation (8) may be written

$$c_p - c_v = \frac{-T.\left(\frac{\partial v}{\partial T}\right)^2}{\frac{\partial v}{\partial p}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

As the volume of a body always diminishes on compression, $\frac{\partial v}{\partial p}$ must always be negative and $c_p - c_v$ positive. It is thus possible to calculate the difference between the specific heats from the compressibility and the coefficient of expansion. This result is important, as it is often only possible to obtain c_p for solids and liquids by direct determination.

An interesting deduction can be made from equation (7) regarding the variation of c_v with the volume. Differentiating (7) with respect to T, we have

$$\frac{\partial^2 U}{\partial v \partial T} = -\frac{\partial p}{\partial T} + T\frac{\partial^2 p}{\partial T^2} + \frac{\partial p}{\partial T} = T\frac{\partial^2 p}{\partial T^2}.$$

But $$\frac{\partial^2 U}{\partial v \partial T} = \frac{\partial \frac{\partial U}{\partial T}}{\partial v} = \frac{\partial c_v}{\partial v},$$

and hence $$\frac{\partial c_v}{\partial v} = T\frac{\partial^2 p}{\partial T^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Thus the specific heat c_v is independent of the volume if $\frac{\partial^2 p}{\partial T^2}=0$, that is, if the temperature coefficient of the pressure is independent of the temperature, or if the pressure at constant volume is a linear function of the temperature. This is the case for perfect gases, for which $p=\frac{RT}{v}$. It is also the case for real gases which obey van der Waals' equation

$$p=\frac{RT}{v-b}-\frac{a}{v^2}.$$

We have seen, however (see p. 71), that the specific heat c_v is dependent on the volume for a number of gases. It follows from this that van der Waals' equation cannot be strictly accurate for them, a conclusion to which we have already had occasion to refer.

The corresponding equation for the variation of the specific heat c_p with pressure can be deduced in a similar manner.

Thus we find

$$\frac{\partial c_p}{\partial p}=-T\frac{\partial^2 v}{\partial T^2}. \quad \text{.....(10}a\text{)}$$

$\frac{d^2p}{\partial T^2}$ and $\frac{d^2v}{\partial T^2}$ are a measure of the curvature of the p, T and v, T curves respectively. The variation of the specific heat with volume, or with pressure is therefore greater the more the substance differs in its behaviour from the perfect gas. It is interesting to note that c_p varies with the pressure for gases which obey van der Waals' equation.

From equation (7) we can derive another important result. The left side of the equation is the quantity of heat which we should have to withdraw from a body in compressing it by unit volume at constant temperature.

For we have $$dQ=dU+p\,dv,$$

and therefore $$\left(\frac{\partial Q}{\partial v}\right)_T=\frac{\partial U}{\partial v}+p,$$

and by (7), $$\left(\frac{\partial Q}{\partial v}\right)_T=T\frac{\partial p}{\partial T}=-T\frac{\frac{\partial v}{\partial T}}{\frac{\partial v}{\partial p}}. \quad \text{.....(11)}$$

The coefficient of expansion $\frac{\partial v}{\partial T}=\alpha$ and the compressibility $-\frac{\partial v}{\partial p}=\varkappa$ can be determined by experiment, and the heat of compression (or dilatation) can then be calculated from them by equation (11).

We may mention here an interesting empirical relationship discovered by Lewis.* He found that $\left(\frac{\partial Q}{\partial v}\right)_T$, which is a measure of the work done against the molecular forces when

Substance.	t° C.	l calc.	l exp.	t_1° C.
Ethylene chloride	0	89·3	85·4	0
Ethyl chloride	0	109	100·1	21
Ethyl bromide	0	65·5	61·65	38
Ethyl iodide	0	52	47	71·3
Methyl acetate	0	94·7	114	0
Ethyl acetate	0	86·9	86·7 102·1	76 0
Benzene	15	98	106	15
Toluene	0	98·3	83·6	111
Xylene	0	95·7	78·25	139
Cymene	0	90·1	66·3	175
Bromine	0	37·3	45·6	58
Mercury	20	24·7	31·37 31·3	20 0
Acetone	0	130	139	0
Carbon disulphide	0	70·4	89·5	0
Ether	0	91·2	94	0
Chloroform	0	57·6	67	0
Carbon tetrachloride	0	48·6	52	0
Methyl alcohol	0	123·6	290	0
Ethyl alcohol	0	117	225	0
n-Propyl alcohol	0	68·7	166	0
Isopropyl alcohol	0	89	161	82
n-Butyl alcohol	0	79·2	143	116
Water	0 4 >4	<0 0 >0	ca. 600	0

the distance between the molecules is increased by a small amount, is very nearly equal to the ordinary latent heat of

* Cf. Wm. C. McC. Lewis, *Zeitschr. f. physikal Chemie*, **78**, 24 (1911).

evaporation (for unit volume of the liquid). In other words, the work done against molecular forces in increasing the volume of a very large amount of a liquid by 1 litre, is equal to the work done against the molecular forces when the molecules of 1 litre of the liquid are removed to an infinite distance apart (evaporated).

Lewis has tested this relationship as far as is possible with the data available in the literature, and finds that it is approximately true for all normal unassociated liquids. For associated liquids, such as water, the alcohols and the organic acids, the observed latent heats are considerably greater than those calculated from the coefficient of expansion and the compressibility. This may be due to the additional work necessary to split up the associated molecules. A deviation from Lewis' rule may therefore be taken as an indication of the association of the liquid, and is perhaps a better criterion than most of the other methods used for this purpose. The table on p. 153 (taken from Lewis' paper) contains the temperature $t°$ for which the latent heat was calculated, the calculated and observed latent heats, and, finally, the temperature $t_1°$ at which the latent heat was determined.

4. The mechanical significance of the second law and of the concept of entropy.

Entropy and probability. The recognition of the universal applicability of the law of the conservation of energy is partly based on the mechanical conception of heat as motion of the ultimate particles of matter. If heat, energy, and kinetic energy of the molecules are essentially of the same nature, and are differentiated from one another only by the units in which we measure them, the validity of the law of the equivalence of heat and work is explained. At first sight, however, it is not easy to understand why heat cannot be converted completely into work, or, in other words, why the conversion of heat into work is an irreversible process (second law of thermodynamics). In pure mechanics we deal only with perfectly reversible processes. By the principles of mechanics the complete conversion of heat into work should be just as possible as the conversion

of work into heat, and yet experience has shown that there is not a single process in nature which results solely in the conversion of heat into work.

The classical researches of Ludwig Boltzmann showed how this apparent contradiction could be explained, and how the mechanical theory of heat could be established on a firm basis, namely, by the hypothesis that heat consists of a chaotic (molecular ungeordnet) motion of the ultimate particles.*

The distinction between ordered and chaotic motion may be illustrated by contrasting the motion of a regiment of soldiers with that of a swarm of gnats (Helmholtz).

This difference may be defined more accurately by the statement that the velocity of each particle is related in some definite and regular manner to the velocity of the neighbouring particles when the motion is ordered, while this is not the case when the motion is chaotic.

In the motion of a material body composed of a large number of molecules, all the molecules have a common component velocity in the direction of motion of the body. If the motion of the body is arrested, by collision with an inelastic screen for example, its kinetic energy is converted into heat, and the ordered motion is converted into chaotic motion of the molecules, the total kinetic energy of the molecules remaining constant. We shall have reconciled the irreversibility of such processes with the principles of mechanics if we can show that in the motion of material bodies the ordered motion always tends of its own accord to become more disordered or chaotic, while chaotic motion never of its own accord becomes more ordered.

Let us consider, for example, a hollow cubical vessel filled half with white and half with black balls, and let the balls be arranged like the squares of a chess-board, so that each white ball is separated by a black ball from the next. If the contents of this cubical vessel are poured into another vessel and then back again into the first, we know by experience that the regularity of the arrangement would in general be destroyed, and that, if we repeat this process several times, it would hardly

* Ludwig Boltzmann, *Gastheorie*. Cf. also M. Planck, *Theorie der Wärmestrahlung*, p. 134 *et seq.*

ever happen that the arrangement of the balls at the end of the process would be the same as at the beginning. The probability of obtaining the original arrangement is less the greater the number of the balls, and is infinitely small if we take an infinite number of balls. In order to reconstruct the original arrangement, it would be necessary to remove the balls from the vessel and replace them one by one, that is to say, we should have to do work on the system. We know by experience that the process of pouring the balls backwards and forwards is an irreversible process like the conversion of work into heat, that is to say, it is a process which cannot be reversed without external compensation.

A second example will facilitate the conception of this principle. Consider a single gaseous molecule moving according to the principles of the kinetic theory in the interior of an empty cubical vessel. By collision with the walls of the vessel the course of the molecule is constantly being altered, and we shall find the molecule at one moment in the one half A of the vessel and at another moment in the other half B. The probability that the molecule shall be in A at any instant is just as great as the probability that it shall be in B. The state of the system in which the molecule is in A will therefore recur frequently, so that the passage of the molecule from A to B is reversible. On the other hand, if we have a large number of molecules moving backwards and forwards in the same vessel, the distribution of the molecules will generally be such that the number of molecules in A and in B is the same. There will, however, always be some instants at which by chance all the molecules are in A or all in B. This state of affairs is, strictly speaking, also reversible, since it recurs after the lapse of an interval of time, but the larger the total number of molecules in the vessel the less frequently will this reversal occur. For a finite mass of gas consisting of an exceedingly large number of molecules the probability that all the molecules shall happen to be in A at the same time, and thus that B is a vacuum, is excessively small. Boltzmann calculated by the laws of probability the number of seconds which would elapse before all the molecules in 1 c.c. of air would return of their own accord to the half A of

the vessel. The number which he obtained has several trillions of digits, and therefore corresponds to an enormous number of millions of years. We are thus well justified in assuming that we shall never be able to observe the spontaneous reversal of the expansion of a gas into a vacuum. In this way we can explain the irreversibility of one of the typical irreversible processes mentioned on p. 130.

We have arrived at this result by applying the laws of probability to the motion of the molecules, *i.e.* by what is known as the statistical method. The justification of this procedure is to be found in those experiences which we express in the law of great numbers, that is, in the statement that the consequences of the calculus of probabilities are more closely in accord with the facts the greater the number of cases observed. In throwing dice the probability of throwing a 6 with a single die is $\frac{1}{6}$ (*i.e.* the number of favourable throws divided by the number of possible throws). In six actual throws, however, we do not always throw one 6; sometimes, however, we may throw a 6 two or three times in succession. The greater the number of throws, the more closely will the ratio of the favourable throws (sixes) to the total number of throws approximate to $\frac{1}{6}$, so that in the limit, for an infinite number of throws, we obtain this ratio exactly. As material bodies are made up of an exceedingly large number of molecules, we conclude that the motions of these molecules will be determined exactly by the laws of probability. The statistical theory of the second law of thermodynamics is based on the hypothesis of the molecular structure of matter, and has therefore a decided superiority over the purely energetic conception of nature.*

All natural systems composed of small particles have therefore a tendency to change from states in which the arrangement of the particles, or of the motions of the particles, are ordered to the state in which there is the greatest molecular disorder or chaos. Stable equilibrium is not attained until the chaos is complete, and until the state of the system has a greater probability than any other possible state. By a possible state

* According to Planck (8 *Vorträge*, Leipzig, 1910, p. 40) the irreversibility of natural processes leads of necessity to an atomistic conception of nature.

of the system we mean any state which is consistent with the external conditions (energy, volume, pressure, etc.) of the system. In all spontaneous processes the probability of the state of the system increases and tends towards a maximum.

We came to the same conclusion before with regard to the entropy of a system, and for this reason Boltzmann arrived at the important conclusion that the entropy S of a system is determined by the probability of the state of its molecular motion, and can be measured by it, so that $S = F(w)$.

Let us examine the conception of the probability of a state of molecular motion a little more closely. Consider N molecules of a perfect monatomic gas at constant temperature. The velocities of the individual molecules may then have any direction or magnitude, but for every distribution of velocities the sum $U = \Sigma \frac{Nmc^2}{2}$, the energy of the gas, must have the same value. This condition can be complied with in a great variety of ways. For example, all the molecules may have the same velocity c; or n_1 of the N molecules may have the velocity c_1, n_2 the velocity c_2, n_3 the velocity c_3, and so on.

But every distribution of this kind, characterised by a definite number and magnitude of different velocities, can again be built up in different ways from the different molecules.

If we designate the molecules by the symbols a_1, a_2, $a_3 \ldots a_N$, and assume only two different velocities c_1 and c_2, we have the following possible distributions (n molecules having the velocity c_1 and $N-n$ the velocity c_2):

1. The molecules a_1, a_2, $a_3 \ldots a_n$ have the velocity c_1 and the remainder have the velocity c_2.
2. The molecules a_2, a_3, $a_4 \ldots a_{n+1}$ have the velocity c_1 and the remainder the velocity c_2.
3. The molecules a_3, $a_4 \ldots a_{n+2}$ have the velocity c_1, and so on.

Taking these distributions of the individual molecules over the various velocities as the favourable cases, and their number, therefore, proportional to the probability of the state under consideration, we find by the rules of the calculus of probability,

assuming only two velocities c_1 and c_2 in our example, that the probability w is given by

$$w = k_1 \frac{N!}{n!(N-n)!}.*$$

The number of favourable cases, and hence the probability, becomes very much greater if, instead of only two different velocities, we take s different velocities c_1, c_2, $c_3 \ldots c_s$. The probability then becomes

$$w = k_1 \frac{N!}{n_1! n_2! n_3! \ldots n_s!}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where $$n_1 + n_2 + n_3 + \ldots + n_s = N.$$

The gas will be in equilibrium at constant energy and constant volume when, for all distributions consistent with the laws of dynamics, the probability is a maximum. Boltzmann has shown that this is the case when the velocities of the molecules are distributed according to Maxwell's law of distribution.

We can now determine the form of the function $S = F(w)$. If we have two systems having the entropies S_1 and S_2, and the probabilities w_1 and w_2, then

$$S_1 = F(w_1),$$
$$S_2 = F(w_2).$$

The entropy of the whole system is then

$$S = S_1 + S_2.$$

The probability that the two systems shall have the probabilities w_1 and w_2 simultaneously is, by a rule of the calculus of probabilities,

$$w = w_1 . w_2.$$

Hence $$S = F(w_1 . w_2) = F(w_1) + F(w_2).$$

This condition can only be complied with by the logarithmic function,

$$F(w) = k \ln w + \text{const.} = S.$$

The value of the constant is so far entirely arbitrary. If, however, we make the assumption that the entropy of a system

* This definition of the probability, which is due to Boltzmann, differs from the ordinary definition, $w = \frac{\text{number of favourable cases}}{\text{number of possible cases}}$, in that the constant denominator is left indeterminate.

is determined only by the probability of the molecular arrangement,* the constant must vanish, and we should have the equation

$$S = klnw.$$

Here k is a constant of universal significance independent of the chemical nature and of the variables of condition of the substance whose entropy is S. All quantities characteristic of the individual substances must therefore be contained in the expression w.

Calculation of the entropy of a perfect gas. The calculation of w in terms of quantities which can be measured experimentally (pressure, volume, temperature), and of the number and mass of the molecules, is accompanied in the general case by very serious difficulties. For a perfect monatomic gas Boltzmann has succeeded in solving the problem, thus calculating the entropy S. For a perfect monatomic gas he deduces from equation (1) the expression †

$$S = \tfrac{3}{2}kNlnU + kNlnv + K. \quad \text{.....(2)}$$

Here U and v are the energy and the volume of a monatomic gas consisting of N molecules. K is a constant independent of the energy and the volume, but involving the number and mass of the molecules, and also depending on the manner in which the probability w is calculated.

With the aid of the thermodynamical relations discussed in the previous paragraph, we can deduce the equation of condition of a monatomic perfect gas. By equation (5), p. 150, we have

$$\frac{\partial S}{\partial \dot{T}} = \frac{1}{T}\frac{\partial U}{\partial \dot{T}},$$

and by (2),

$$\frac{\partial S}{\partial T} = \tfrac{3}{2}kN\frac{1}{U}\frac{\partial U}{\partial T},$$

and hence

$$U = \tfrac{3}{2}kNT. \quad \text{.....(3)}$$

Equation (3) is identical with the relation between the energy and the temperature of a gas which we derived, on p. 86, from Gay-Lussac's law, *i.e.* from experiment.

* See Planck, *Wärmestrahlung*, p. 135 (1st edition).

† See Planck, *Wärmestrahlung*, p. 145 (1st edition).

Comparing the two equations, we have, for 1 mol. of the gas,

$$U = \tfrac{3}{2}RT = \tfrac{3}{2}kNT,$$

and hence for the gas constant,

$$R = k \,.\, N, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3a)$$

and for the specific heat, $c_v = \dfrac{\partial U}{\partial T} = \tfrac{3}{2}R$, where N is Loschmit's value for the number of molecules in 1 mol.

Planck was able to calculate the value of N by equation (3a) from the gas constant R, and the value of the universal constant k, which he deduced from the laws of radiation. The value which he obtained agrees excellently with those calculated in other totally different ways. This agreement is very remarkable, and is a confirmation of the correctness of the equation $S = klnw$.

By equation (6), p. 150, we have

$$\frac{\partial S}{\partial v} = \frac{1}{T}\left(\frac{\partial U}{\partial v} + p\right),$$

and by equation (2) (for 1 mol. of gas),

$$\frac{\partial S}{\partial v} = \frac{kN}{v} = \frac{R}{v}.$$

As $\dfrac{\partial U}{\partial v} = 0$, by equation (3$a$), we have at once, for a perfect gas,

$$pv = RT. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Basing our calculation on the relationship between entropy and probability, we have thus been able to deduce the complete equation of condition for a perfect gas from the kinetic theory. Transforming equation (2) by means of (3) and (3a), and remembering that, for a perfect gas, $\tfrac{3}{2}R = c_v$, we have, for the entropy per mol.,

$$S = c_v lnT + Rlnv + K'.$$

This is in complete agreement with the thermodynamical expression on p. 143 if we put $K' = S'$.*

* For the calculation of the entropy constant S' from kinetic considerations, see O. Sackur, *Ann. d. Physik*, **36**, 958.

Strictly speaking, the equation $K' = S'$ is an extension of Boltzmann's theory, in so far as we have ascribed a definite value to the entropy constant. According to Boltzmann, the probability contains an undetermined factor, which cannot be evaluated without the introduction of new hypotheses. Boltzmann and Clausius suppose that the entropy may assume any positive or negative value, and that the change in entropy alone can be determined by experiment. Of late, however, Planck, in connection with Nernst's "heat theorem," has stated the hypothesis that the entropy has always a finite positive value, which is characteristic of the chemical behaviour of the substance. The probability must then always be greater than unity, since its logarithm is a positive quantity. The thermodynamical probability is therefore proportional to, but not identical with, the mathematical probability, which is always a proper fraction. The definition of the quantity w on p. 159 satisfies these conditions, but so far it has not been shown that this definition is sufficient under all circumstances to enable us to calculate the entropy.

Planck is of opinion that the assumption that the entropy is always a positive quantity, and hence that the probability is always an integer, is equivalent to the so-called quantum hypothesis.*

So far, our equations apply only to monatomic gases. The behaviour of polyatomic gases can, however, also be explained by the kinetic theory. We showed on p. 95 that the total energy of a polyatomic gas consists not only of the kinetic energy of the translational motion, but also partly of the internal energy of the molecules. It is natural to assume that the atoms are capable of motion inside the molecule, and are therefore endowed with intramolecular kinetic energy. By making certain hypotheses as to the nature of these intramolecular motions, we are able to calculate the specific heats of polyatomic gases.

Some of the more important hypotheses of this kind are as follows:

(1) Boltzmann assumes that the atoms in diatomic mole-

* Planck, *Wärmestrahlung*, 2nd edition. See also O. Sackur, *Jahr. Ber. d. Schles. Gesellsch. f. Vaterl. Kultur*, 1913.

cules (such as O_2, N_2, etc.) are connected rigidly with one another, and are capable of rotating about an axis perpendicular to the line joining them, or

(2) That vibrational motion can take place in a fixed direction in the molecule.

Both hypotheses lead to the entropy equation

$$S = \tfrac{5}{2} R \ln U + R \ln v + S',$$

and hence to the equations $U = \tfrac{5}{2} RT$, $c_v = \tfrac{5}{2} R$, and $\frac{c_p}{c_v} = \frac{7}{5}$, which are true for many diatomic gases (O_2, N_2, CO).

(3) That in triatomic molecules rotations may take place about three different axes. From this we deduce $U = 3RT$, $c_v = 3R$, and $\frac{c_p}{c_v} = \frac{4}{3}$. (This holds for H_2O vapour at not too high temperatures.)

(4) Maxwell assumed that the atoms were free to move in all three directions of space without destroying the integrity of the molecule.

On this assumption the ratio of the specific heats even for diatomic gases is $\frac{4}{3}$, which is actually the case for certain gases, such as chlorine.

All these calculations are based on the assumption that the total energy is uniformly distributed according to the laws of probability over all the different kinds of motion (degrees of freedom), and they all agree in making the specific heat of gases independent of the temperature. This result is, however, only confirmed in the case of monatomic gases, such as argon.* For permanent diatomic gases (O_2, N_2, H_2, CO) the variation of the specific heat with the temperature is also very small, but, nevertheless, distinctly perceptible.

Easily liquefiable diatomic gases (Cl_2), and all tri- and poly-atomic gases, show a very distinct increase of both specific heats with the temperature. It would seem that our present theory of gases breaks down here utterly, and the failure of the theory becomes more apparent as we go to higher and higher temperatures. The deviations of real gases from the gas laws, which we discussed earlier in the book, are of a totally different

* Pier, *Zeitschr. f. Elektrochemie*, **16**, 897 (1910).

character from those which we are now discussing. The former can be accounted for by Van der Waals' equation, and the disagreement with theory becomes less and less as we increase the temperature or the mean free path of the molecules. The abnormal behaviour of the specific heats has not yet been explained satisfactorily. Nernst was the first to point out that this deficiency in the classical theory could be supplied by means of the quantum hypothesis. According to this hypothesis, the energy of vibration of the atoms inside the molecule must increase more rapidly with the temperature than their translational energy, so that the part of the specific heat which is due to the intramolecular energy varies with the temperature.* The rapid decrease in the specific heat of hydrogen at low temperatures can also be accounted for in this way.†

Entropy of solid bodies. In the same manner as we calculated the entropy of a perfect gas, we can calculate the entropy of a solid body, if we assume Einstein's theory that the atoms in the solid vibrate with a frequency which is independent of the temperature and volume, and that the energy of the vibration is always an integral multiple of the quantum of energy

$$h\nu = \beta\nu \cdot \frac{R}{N}$$

(see p. 34).‡

The entropy is then equal to the entropy of an electromagnetic resonator of frequency ν capable of vibrating in all three directions of space. According to Planck's theory this leads to the equation :

$$S = 3k\Sigma N \left[\frac{e^{\frac{\beta\nu}{T}}}{e^{\frac{\beta\nu}{T}} - 1} \cdot \frac{\beta\nu}{T} - ln\left(e^{\frac{\beta\nu}{T}} - 1\right) \right]. \quad \ldots\ldots\ldots\ldots (5)$$

For substances composed of several vibrating systems of different frequency, the summation is to be extended over all the values of ν.

* Nernst, *Zeit. f. Elektrochemie*, **17**, 265 (1911).

† See also Einstein and O. Stern, *Ann. d. Physik*, **40**, p. 551, 1913; and O. Sackur, *loc. cit.*

‡ Eucken (*Ber. d. Berl. Akad.* 1912, p. 141). For hydrogen at 60° abs. $c_v = 3$, which is the value for a monatomic gas.

This equation leads us to some important and strikingly simple results, much as we were led to draw conclusions as to the physical behaviour of perfect gases from their entropy equation. In analogy with the term "perfect gas," the author proposes the term "perfect solid" * for substances which conform to Einstein's assumptions.

From (5) we have

$$\frac{\partial S}{\partial v} = 0.$$

The entropy of a perfect solid is therefore independent of its volume. From this it follows that if solid solutions can be formed at all, no diffusion can take place in them.

Further, combining (5) with equation (6) on p. 150, we have

$$\frac{\partial U}{\partial v} + p = 0,$$

and hence for the differential of the total energy,

$$dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv = c_v dT - p\, dv.$$

As dU is a complete differential, it follows that

$$\frac{\partial c_v}{\partial v} = \frac{\partial p}{\partial T} = 0,$$

since c_v is a function of ν and T alone, and is independent of v (see p. 34). From this it also follows that

$$\frac{\partial v}{\partial T} = 0 \quad \text{and} \quad \frac{\partial v}{\partial p} = \text{const.},$$

i.e. independent of the temperature. Hence also

$$c_p = c_v.$$

The significance of these equations is as follows: The coefficient of expansion of a perfect solid body is zero, and its compressibility is independent of the temperature. In the compression of a perfect solid, no rise in temperature is produced. The work done in the compression does not contribute to the kinetic energy of the atoms and merely increases their potential energy.

* O. Sackur, *Ann. d. Physik*, **34**, 465 (1911).

If we compare the actual behaviour of solid bodies with those of the hypothetical perfect solid, we find that the coefficient of expansion is very small for all solids, and appears to approach zero as we diminish the temperature (according to Thiesen,* Gruneisen,† and Lindeman ‡). The variation of compressibility with temperature is also very small, and appears likewise to approach zero as the temperature is diminished. §

Real solid bodies, therefore, differ considerably from the perfect solid at higher temperatures, but appear to approach asymptotically to the " perfect " condition as the temperature is lowered. The conception of a perfect solid body like that of a perfect gas is only true in the limiting case. It will, perhaps, be possible to build up a complete theory of the solid state on the basis of Einstein's hypothesis, as van der Waals' theory was evolved from the conceptions of the classical theory of gases. ||

* *Verh. d. deutsch. physik. Ges.* **10**, 410 1908.

† *Ann. d. Phys.* **33**, 33, 1910.

‡ *Physikal. Zeitschr.* **12**, 1197, 1911. § Gruneisen, *loc. cit.* p. 75.

|| Gruneisen has calculated some of the consequences of the theory, assuming that the frequency ν is a function of the volume v, but independent of the temperature (*Zeit. f. Elektrochem.* **17**, 732, 1911). See also Haber, *Verh. der deutsch. physik. Gesellsch.* **13**, 1117, 1911. An important advance in the theory of the perfect solid is due to Debye (see Chap. II. p. 37).

CHAPTER VI.

THERMODYNAMIC EQUILIBRIUM IN GENERAL. THERMODYNAMIC FUNCTIONS.

1. Introduction. Systems subject to conditions of constraint.

In the last chapter we showed that an isolated system is in equilibrium when its entropy is a maximum. In chemistry and physics, however, most of the systems with which we have to deal are not isolated, and it is therefore a question of importance to determine under what circumstances a system will be in equilibrium when its interaction with the surroundings is prescribed in some definite manner.

Conditions which restrict the way in which a system may vary are called conditions of constraint, or more briefly constraints. Systems are usually named according to the nature of the constraints; thus the condition of constraint for an isothermal system is that its temperature shall not vary; for an isodynamic system, that its total energy shall not vary, and so forth. Conditions of constraint can always be expressed mathematically by means of equations between the variables which determine the state of the system, or between the differentials of these variables.

In the following, if f is a function of the variables which determine the state of a system, the amount by which f is increased by any possible infinitesimal change of state will be denoted by δf. The constraints to which the variation is subject will often be indicated by suffices; thus

$$(\delta f)_T = 0$$

means that for any possible infinitesimal change of state which

leaves the temperature of the system unaltered, the increase in the function f is zero. In other words, the function f is either a maximum or a minimum for isothermal changes. In order to distinguish between a maximum and a minimum, we shall employ the inequality sign in the following manner:

For a maximum of f we shall write

$$\delta f \leqq 0,$$

which may be read "all possible variations in the state of the system involve a diminution or no change in the function f."

For a minimum we shall write

$$\delta f \geqq 0,$$

which may be interpreted in a similar manner.

If we restrict ourselves to reversible variations in the state of the system, we may write the first law of thermodynamics in the form

$$dU = T\,dS - dw, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where dU is the differential of the total energy of the system, dS the differential of its entropy, and dw is the differential amount of work done by the system on the surroundings. It is important to remember that equation (1) applies only to reversible processes.

The work done dw may be of any kind (*e.g.* electrical, osmotic, expansion against pressure, etc.), or may be a sum of several of these kinds of work, say $\Sigma\pi\,d\rho$ in which case we may write the first law in the form

$$dU = T\,dS - \Sigma\pi\,d\rho. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

2. Isolated and isodynamic systems.

A system cannot be isolated if it is subject to constraints which necessitate interaction with some other system or systems. Any system, however, taken together with all the other systems with which it interacts, forms an isolated system.

It follows from the second law (see Chap. V. p. 144) that such an isolated system is in equilibrium if no possible reversible variation in its state can yield work to the surroundings.

Since the internal energy of an isolated system or of an iso-

dynamic system is constant, we have as a "condition of constraint" $\delta U = 0$. Equation (1) therefore reduces in this case to

$$T(\delta S)_U = (\delta w)_U.$$

The system is in equilibrium when $(\delta w)_U$ is zero or negative, *i.e.* when

$$T(\delta S)_U \leqq 0.$$

Since T is always positive, this is equivalent to

$$(\delta S)_U \leqq 0. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

In words: *The system is in equilibrium when its entropy is a maximum.* We are already familiar with this result.

3. Isentropic systems.

All purely mechanical systems belong to this class. An isentropic system might be isolated in addition if all changes which it underwent were perfectly reversible. Thus a perfectly frictionless spinning-top is an example of an isolated isentropic system. Such systems, of course, are pure abstractions and do not occur in nature. Actual isentropic systems must increase the entropy of their surroundings if they change at all, since the system and the surroundings together form an isolated system. An isentropic system can always increase the entropy of its surroundings, and can only do so when it is capable of doing work; for work can always be converted into heat, and the entropy of all bodies is increased when they absorb heat.

Since the entropy of an isentropic system is constant by definition, we have as a condition of constraint $\delta S = 0$. In this case the first law (equation 1) becomes

$$(\delta U)_S = -(\delta w)_S.$$

We have just shown that an isentropic system cannot change, and is therefore in equilibrium when it is incapable of doing work on its surroundings, *i.e.* when $(\delta w)_S$ is zero or negative.

We have therefore $(\delta U)_S \geqq 0$ ..... (4)

as the condition for equilibrium. An isentropic system is therefore in equilibrium when its internal energy is a minimum.

As an illustration, let us consider a mol of a perfect gas. Here

$$U = c_v T = c_v T_0 \left(\frac{v_0}{v}\right)^{k-1} = c_v T_0 \left(\frac{p}{p_0}\right)^{\frac{k-1}{k}},$$

where $k = \frac{c_p}{c_v}$. Since $k-1$ is positive, the internal energy can always be diminished by increasing v or by diminishing p. The gas therefore cannot be in equilibrium if it is free to expand. If we enclose the gas in a rigid envelope of volume V, it is in equilibrium when it occupies this volume completely, for then every possible variation in its state is accompanied by an increase in its internal energy.

This is a good illustration of what is meant by a *possible* variation, *i.e.* a variation consistent with the nature and constraints of the system. Thus expansion to a volume slightly greater than V would not be a *possible* variation.

4. Isentropic-isopiestic systems. The heat-content function.

If we suppose a system to be capable of changing in volume at constant entropy and keep the pressure on the system constant, then work will be done against this constant pressure whenever the volume increases. The system by itself is therefore not isolated, since it does work on some other systems (*e.g.* the atmosphere or a weighted piston) which serves to maintain the constant pressure. Since the manner in which the constant pressure is exerted can have no effect on the equilibrium of the system, we may suppose the pressure regulator to be isolated from everything but the system on which it exerts the pressure. The system and the pressure regulator combined then form an isentropic system, and are therefore in equilibrium when they are together incapable of doing work. The work done on the surroundings by the combined system is the total work done by the isentropic-isopiestic system, less the work done on the pressure regulator. The first law in this case becomes

$$(\delta U)_{S,p} = -p(\delta v)_{S,p} - (\delta w)_{S,p},$$

where U is the energy of the isentropic-isopiestic system (not of the combined system including the pressure regulator), v is its volume and $(\delta w)_{S,p}$ is the work done on the surroundings.

For equilibrium therefore $(\delta w)_{S,p}$ must be zero or negative, and hence

$$(\delta U)_{S,p} + p(\delta v)_{S,p} \geqq 0$$

is the condition for equilibrium.

If we define the function H by the equation

$$H = U + pv,$$

we have, by differentiation,

$$(\delta H)_{S,p} = (\delta U)_{S,p} + p(\delta v)_{S,p},$$

and hence the equilibrium condition may be written in the form

$$(\delta H)_{S,p} \geqq 0. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

For any finite change of state carried out reversibly at constant entropy and pressure, we have

$$\int_1^2 dH = \int_1^2 dw,$$

or

$$w = H_2 - H_1.$$

Isentropic-isopiestic systems are of no great practical importance, and the chief value of the function H lies in its relationship to the heat of reaction at constant pressure, Q_p. Suppose that we allow a chemical system to react at the atmospheric pressure, in such a manner that the only work done is that due to the change in the volume of the system.

We have then, by the first law,

$$U_2 - U_1 = Q_p - p(v_2 - v_1),$$

and hence

$$\begin{aligned} Q_p &= (U_2 + pv_2) - (U_1 + pv_1) \\ &= H_2 - H_1. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6) \end{aligned}$$

The heat of reaction at constant pressure is therefore equal to the change in the function H. For this reason H is called the heat content of the system, or the heat function for constant pressure.

5. Isothermal systems. The free-energy function.

All that is necessary to maintain constant temperature in a system is to place it in a thermostat. In essence a thermostat is a system which can absorb or give out indefinite amounts of heat without changing in temperature. Thus a mixture of ice and

water may be used as a thermostat. Most thermostatic substances change slightly in volume when they absorb or give out heat, and therefore do a certain amount of work against the pressure of the atmosphere. It is, however, possible to construct thermostats which do no work when they absorb or give out heat. Thus an indefinitely large mass of any substance whose coefficient of expansion is zero (such as fused silica at the point of maximum density, or water at 4° C.) is a thermostat of this kind.

We can now always combine our isothermal system with such a thermostat, so that the two together form an isolated system. The second law tells us that any spontaneous change of state in this isolated system must be of such a nature that if carried out reversibly it will yield work. Since the thermostat can neither do nor consume work, the whole system will be in equilibrium when the isothermal system is incapable of doing work.

In this case the first law tells us that

$$(\delta U)_T = T(\delta S)_T - (\delta w)_T,$$

where the variations refer to the energy, entropy and work done by the isothermal system alone. For equilibrium δw_T must be either zero or negative, and hence

$$(\delta U)_T - T(\delta S)_T \geqq 0$$

is the condition for equilibrium.

Defining the free energy function by the equation

$$\psi = U - TS,$$

we have, by differentiation at constant temperature,

$$(\delta\psi)_T = (\delta U)_T - T(\delta S)_T,$$

so that the equilibrium condition may be written in the form

$$(\delta\psi)_T \geqq 0. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

In words: An isothermal system is in equilibrium when its free energy is a minimum. All spontaneous processes in an isolated system involve a diminution in its free energy.

As an illustration, let us take again a mol of a perfect gas.

Here we have

$$U = c_v T,$$
$$S = c_v \ln T + R \ln v + S_1,$$

and hence

$$\psi = U - TS$$
$$= (c_v - S_1) T - c_v T \ln T - RT \ln v.$$

For isothermal changes, since T is constant,

$$\psi = -RT \ln v + \text{const.}$$

The free energy can therefore always be diminished by increasing the volume, so that a perfect gas can never be in equilibrium if it is free to expand isothermally. If the gas is contained in a rigid vessel immersed in a thermostat, it will fill the vessel completely, since this is the greatest volume at its disposal under the circumstances.

If a mol of a gas at volume v_1 is allowed to expand in a thermostat into an evacuated vessel, thus increasing its volume to v_2, the change in free energy is

$$\psi_1 - \psi_2 = RT \ln \frac{v_2}{v_1},$$

which is the work done when the gas expands isothermally and reversibly from v_1 to v_2.

In general, the difference between the free energies of a system in two states at the same temperature is the work done when the system is made to go isothermally and reversibly from the one state to the other. For we have

$$w_T = \int_1^2 dw_T = -\int_1^2 d\psi_T = \psi_1 - \psi_2.$$

Since $\psi_1 - \psi_2$ is dependent only on the values of the variables of state at the beginning and end of the process, it follows that the work done by the system is the same for all reversible and isothermal processes, which bring the system from state 1 to state 2.

6. Isothermal - isopiestic systems. The thermodynamic potential.

In chemistry we often have to deal with systems which are exposed to the pressure of the atmosphere or to some constant

pressure during the processes which we are studying. The temperature of such a system may be kept constant, as in the preceding case, by means of a thermostat which absorbs and gives out heat without doing work; but the system and thermostat do not yet form an isolated system, since work is necessarily done when the volume of the system changes. We may, however, suppose the pressure to be kept constant by means of an otherwise isolated pressure regulator as in section 4. The isothermal-isopiestic system, the thermostat, and the pressure regulator now constitute an isolated system. Since neither the thermostat nor the pressure regulator can do work on the surroundings, the second law tells us that any spontaneous change in the state of the combined system must be of such a nature that if executed reversibly it will necessitate the doing of work by the isothermal-isopiestic system, in excess of that which is done on the pressure regulator.

The first law in this case may be stated in the form

$$(\delta U)_{T,p} = T(\delta S)_{T,p} - p(\delta v)_{T,p} - (\delta w)_{T,p},$$

where the variations, as before, refer only to the isothermal-isopiestic system, and $(\delta w)_{T,p}$ is the work done by the system in excess of that which it does on the pressure regulator. For equilibrium $(\delta w)_{T,p}$ must therefore be either zero or negative (since it is the work done by the combined system on the surroundings), and hence

$$(\delta U)_{T,p} - T(\delta S)_{T,p} + p(\delta v)_{T,p} = 0.$$

Defining the thermodynamic potential by the equation

$$\zeta = U - TS + pv,$$

we have, by differentiation,

$$(\delta \zeta)_{T,p} = (\delta U)_{T,p} - T(\delta S)_{T,p} + p(\delta v)_{T,p},$$

and we may therefore write the equilibrium condition in the form

$$(\delta \zeta)_{T,p} \geqq 0. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

In words: An isothermal-isopiestic system is in equilibrium when its thermodynamic potential * is a minimum.

* Some authors use the term free energy for the function ζ, although this term was invented by Helmholtz for the function ψ (see G. N. Lewis, *J. Am. Chem. Soc.* **35**, 14 (1913)).

The same line of reasoning may be extended to isothermal systems composed of various parts, each at a constant but different pressure. If the constant pressures of these parts are $p_1, p_2, \dots p_n$, then the work done by the system on the pressure regulators is $\sum_1^n p_1 \delta v_1$, where v_1 is the volume of the part at pressure p_1, and so on.

In this case the work done δw by the combined system on the surroundings is given by

$$-(\delta w)_{T, p_1, p_2, \dots p_n} = (\delta U)_{T, p_1, p_2, \dots p_n} - T(\delta S)_{T, p_1, p_2, \dots} + \sum_1^n p_1 \delta v_1.$$

Denoting by ξ the function $U - TS + \sum_1^n p_1 v_1$,* we obtain the equilibrium condition in the form

$$(\delta \xi)_{T, p_1, p_2, \dots p_n} \geqq 0.$$

The meaning of the function H (section 4) can be extended in the same way to apply to systems composed of various parts at the pressures $p_1, p_2, \dots p_n$. H would then be defined by the equation

$$H = U + \sum_1^n p_1 v_1.$$

The thermodynamic potential may be defined in terms of H and ψ by the equations

$$\zeta = H - TS,$$

or

$$\xi = \psi + \sum_1^n p_1, v_1.$$

7. Systems of variable chemical composition. Chemical potentials.

In the preceding sections we have derived the thermodynamic conditions for the equilibrium of a system under several different types of constraint. The method of attack has been the same in every case, *i.e.* to suppose the system isolated by combination with such other systems (thermostats, pressure regulators) as may be necessary to enable it to comply with the conditions of constraint. The second law then tells

* See G. N. Lewis (*loc. cit.*).

us that this combined system is in equilibrium when any possible variation in its state is such that the reversible execution of the same variation involves consumption of work from the surroundings.

We shall now consider a more specific class of system to which ordinary chemical solutions (solid, liquid or gaseous) belong. The state of these systems will be considered to be determined when the temperature T, the pressure p and the masses m_1, $m_2 \ldots m_n$ of the substances which compose the system (or solution) are given. Thus the state of a solution of sodium chloride is determined when T, p, the mass of H_2O and the mass of NaCl, are given.

We shall further limit the discussion, in the first instance, to homogeneous systems, that is, to systems in which any portion of a given size and shape taken at random in the system is indistinguishable from any other portion of the same size and shape. This excludes heterogeneous systems such as liquid water in presence of its vapour.

We shall suppose the system (solution) to be maintained at constant temperature and pressure, and shall therefore furnish it with a thermostat and pressure regulator as before. The combined system is, however, not yet isolated, for we shall suppose the solution to be capable of receiving or losing amounts of the various component substances, whose masses m_1', m_2', $\ldots$ m_n' determine its composition.

In order to obtain a completely isolated system, we shall therefore suppose the solution to derive any change in the amounts of its component substances from a second solution containing the masses m_1'', m_2'', $\ldots$ m_n'' of the same components. For the sake of distinction we shall call the first system *solution A* and the second system *solution B*. We shall keep the temperature and pressure in B at the same constant values as in A by means of an additional thermostat and pressure regulator. Solution A and solution B, together with the thermostats and pressure regulators, now form an isolated system.

Let us first consider the simple case in which only one of the components (say the component I, whose mass in A is m_1') is capable of passing from B to A. In other words, we shall

suppose $m_2', \ldots m_n'$, and hence also m_2'', m_3'', $\ldots m_n''$ to be invariable. Suppose now that the mass δm_1 of component I can pass spontaneously from B to A (the combined system remaining completely isolated, and therefore doing no work on the surroundings). The second law tells us that we can gain work from the combined system by transforming δm_1 reversibly from B to A. Let us calculate the amount of work which we can obtain in this way. Let the energy, entropy and volume of solution A be U', S' and v', and let those of B be U'', S'' and v''. We have then, by the first law,

$$\delta(U'+U'')_{T,\,p,\,\substack{m_2'\ldots m_n'\\ m_2''\ldots m_n''}} = T\delta(S'+S'')_{T,\,p,\,\substack{m_2'\ldots m_n'\\ m_2''\ldots m_n''}} - p\delta(v'+V'')_{T,\,p,\,\text{etc.}} - (\delta w)_{T,\,p,\,\text{etc.}},$$

and hence

$$\begin{aligned} -(\delta w)_{T,\,p,\,\text{etc.}} &= \delta(U'-TS'+pv')_{T,\,p,\,\text{etc.}} + \delta(U''-TS''+pv'')_{T,\,p,\,\text{etc.}} \\ &= (\delta\xi')_{T,\,p,\,\substack{m_2'\ldots m_n'\\ m_2''\ldots m_n''}} + (\delta\xi'')_{T,\,p,\,\substack{m_2'\ldots m_n'\\ m_2''\ldots m_n''}}, \end{aligned}$$

where ξ' is the thermodynamic potential of A and ξ'' that of B.*

The thermodynamic potentials of A and B are now, however, dependent not only on the temperature and pressure, but also on the masses of their components. In other words, ξ' is a function of T, p, m_1', m_2', $\ldots m_n'$ and ξ'' is a function of T, p, m_1'', m_2'', $\ldots m_n''$. We have therefore, in general,

$$d\xi' = \frac{\partial\xi'}{\partial T}dT + \frac{\partial\xi'}{\partial p}dp + \frac{\partial\xi'}{\partial m_1'}dm_1' + \frac{\partial\xi'}{\partial m_2'}dm_2' + \ldots + \frac{\partial\xi'}{\partial m_n'}dm_n'$$

and

$$d\xi'' = \frac{\partial\xi''}{\partial T}dT + \frac{\partial\xi''}{\partial p}dp + \frac{\partial\xi''}{\partial m_1''}dm_1'' + \frac{\partial\xi''}{\partial m_2''}dm_2'' + \ldots + \frac{\partial\xi''}{\partial m_n''}dm_n''.$$

* The same result can be obtained more simply as follows: Since the system $A+B$ is an isothermal-isopiestic system, the work done in any reversible change is

$$-(\delta w)_{T,p} = (\delta\zeta)_{T,p}.$$

But the thermodynamic potential of $A+B$ is the sum of the thermodynamic potentials of A and B. Hence

$$-(\delta w)_{T,p} = (\delta\zeta')_{T,p} + (\delta\zeta'')_{T,p}.$$

This is true for any variation at constant temperature and pressure, and hence also for the variation considered in the text, in which case

$$-(\delta w)_{T,\,p,\,\substack{m_2'\ldots m_n'\\ m_2''\ldots m_n''}} = (\delta\zeta')_{T,\,p,\,\substack{m_2'\ldots m_n'\\ m_2''\ldots m_n''}} + (\delta\zeta'')_{T,\,p,\,m_2',\,\text{etc.}}$$

In the present case p, T, m_2', ... m_n', m_2'' ... m_n'' are all constant, while m_1' increases in A by δm_1 and m_1'' diminishes in B by the same amount. All the differentials in the above equations are therefore zero except those of m_1' and m_1'', which are respectively $dm_1' = \delta m_1$ and $dm_1'' = -\delta m_1$.

We have therefore

$$d\zeta' = \frac{\partial \zeta'}{\partial m_1} \delta m_1,$$

$$d\zeta'' = -\frac{\partial \zeta'}{\partial m_1''} \delta m_1.$$

Substituting these values, we obtain for the work done in the reversible transference of δm_1 from B to A,*

$$-\delta w = \left(\frac{\partial \zeta'}{\partial m_1'} - \frac{\partial \zeta''}{\partial m_1''} \right) \delta m_1.$$

We shall call the quantities $\frac{\partial \zeta'}{\partial m_1'}$ and $\frac{\partial \zeta'}{\partial m_2'}$ the chemical potentials of the component I in A and B respectively, and shall denote them by the symbols μ_1' and μ_1''. We have therefore

$$-\delta w = (\mu_1' - \mu_1'') \delta m_1.$$

We have assumed the positive amount δm_1 to be capable of passing spontaneously from B to A, and hence δw must be positive by the second law. We have therefore

$$(\mu_1' - \mu_1'') \delta m_1 < 0;$$

and since δm_1 is positive, this is equivalent to

$$\mu_1' - \mu_1'' < 0 \quad \text{or} \quad \mu_1' < \mu''.$$

Hence the component I can go spontaneously from B to A if its chemical potential in A is less than its chemical potential in B.

The system is in equilibrium if δw is negative or zero for all possible reversible variations in its state. This is the case when

$$(\mu_1' - \mu'') \delta m_1 \gtreqless 0. \quad \text{.....(9)}$$

for any value of δm_1, positive or negative. This can only be the case when

$$\mu_1' = \mu_1'',$$

* The suffices will be omitted in future when there is no danger of confusion.

for if μ_1' were not equal to μ_1'' the difference $\mu_1' - \mu_1''$ would be either positive or negative, and we should always be able to violate the condition (9) by taking δm_1 with the opposite sign to $\mu_1' - \mu_1''$.

So far we have not specified the units in which the quantities $m_1, m_2, \ldots m_n$ are to be measured. In chemistry it is usual to take the mol of each component as the unit of mass, and we may then define the chemical potential $\mu_1' = \frac{\partial \xi'}{m_1}$ of the component I in the solution A as the change in the thermodynamic potential of a very large mass of A when 1 mol of the component I is added to it without changing the temperature, the pressure or the masses of the other components.*

Since the thermodynamic potential is a function of the variables p, T, m_1, $m_2 \ldots m_n$, the chemical potential is also, in general, a function of these variables. We might therefore be led to think that the chemical potentials depend on the amount of the solution which we happen to take, and this again would mean that the equilibrium would vary with the total mass of the solution, a conclusion which is contrary to the facts. It is, however, easy to show that the values of the potentials are independent of the size of the solution.†

Let us define the mol fractions $\nu_1, \nu_2, \ldots \nu_n$ of the component substances in the solution by the equations

$$\nu_1 = \frac{m_1}{m_1 + m_2 + \ldots m_n} = \frac{m_1}{M}, \quad \nu_2 = \frac{m_2}{M}, \ldots \nu_n = \frac{m_n}{M},$$

where M is the total mass of the solution. The quantities $\nu_1, \nu_2, \ldots \nu_n$ are independent of the size of the solution, since the numerators and the denominators are increased in the same ratio when the bulk of the solution is increased. They are, moreover, not all independent, but are connected by the relationship

$$\nu_1 + \nu_2 + \ldots + \nu_n = 1. \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

This may easily be demonstrated by substituting the above values of the mol fractions in equation (10). Hence, if $n-1$ of

* Some authors use the term partial molal free energy for the quantity defined in this way. This term was invented by G. N. Lewis (*loc. cit.*).

† It is assumed here that the effect of surface tension can be neglected, and hence that the size of the solution is sufficiently great to justify this assumption.

the mol fractions are given, the nth can be calculated by means of equation (10).

We shall therefore have proved our point if we can show that the chemical potentials are dependent only on the temperature, the pressure, and the mol fractions of the components.

Since the energy, entropy and volume of M mols of a solution are each equal to M times the energy, entropy and volume of 1 mol of the solution, it follows from the defining equation of the thermodynamic potential ($\xi = U - TS + pv$) that the thermodynamic potential of M mols of the solution is equal to M times the thermodynamic potential of 1 mol of the solution.* We have therefore

$$\xi(p, T, m_1, m_2, \dots m_n) = M\xi_0(p, T, \nu_1, \nu_2, \dots \nu_n),$$

where $\nu_1, \nu_2, \dots \nu_n$ are the masses of the components in 1 mol of the solution, *i.e.* the mol fractions. Hence

$$\mu_1 = \frac{\partial(M\xi_0)}{\partial m_1} = \xi_0 + M\frac{\partial \xi_0}{\partial m_1}.$$

By (10), however, one mol fraction, say ν_n, may be eliminated, so that ξ_0 may be expressed as a function of $\nu_1, \nu_2, \dots \nu_{n-1}$. Hence

$$\begin{aligned}\mu_1 &= \xi_0 + M\left(\frac{\partial \xi_0}{\partial \nu_1}\frac{\partial \nu_1}{\partial m_1} + \frac{\partial \xi_0}{\partial \nu_2}\frac{\partial \nu_2}{\partial m_1} + \dots + \frac{\partial \xi_0}{\partial \nu_{n-1}}\frac{\partial \nu_{n-1}}{\partial m_1}\right) \\ &= \xi_0 + (1-\nu_1)\frac{\partial \xi_0}{\partial \nu_1} - \nu_2\frac{\partial \xi_0}{\partial \nu_2} \dots - \nu_{n-1}\frac{\partial \xi_0}{\partial \nu_{n-1}},\end{aligned}$$

with similar equations for $\mu_2, \mu_3, \dots \mu_n$.

The potentials are therefore completely determined by the temperature, the pressure and the mol fractions of the components, and are thus independent of the size of the solution.

In chemistry it is often expedient to express the concentrations of the components in mols per litre of the solution instead of in mol fractions. If $c_1, c_2, \dots c_n$ are the concentrations in mols per litre, we have

$$\nu_1 = \frac{c_1}{c_1 + c_2 + \dots + c_n} = \frac{1}{1 + \frac{c_2}{c_1} + \frac{c_3}{c_1} + \dots + \frac{c_n}{c_1}},$$

* This is, however, only true when M is not too small, so that surface tension can be neglected.

with $n-1$ similar equations for $\nu_2, \nu_3, \ldots \nu_n$. The mol fractions can therefore be expressed in terms of the $n-1$ ratios of the concentrations $c_1, c_2, \ldots c_n$. It follows, therefore, that the chemical potentials are completely determined by the temperature, the pressure and the $n-1$ ratios of the concentrations in mols per litre.

Let us now consider the general case in which any of the components can pass from solution A to solution B or *vice versa*. By the same reasoning as before we obtain for the work done, when the quantities $m_1, m_2, \ldots m_n$ are brought reversibly from B to A or from A to B,

$$-\delta w = \delta\zeta' + \delta\zeta''.$$

The masses of all the components are now variable in either solution, but since the total amount of each component is invariable we have

$$\begin{aligned} dm_1'' &= -\delta m_1, \; dm_1' = \delta m_1, \\ dm_2'' &= -\delta_2 m, \; dm_2' = \delta m_2, \\ &\ldots\ldots\ldots\ldots\ldots\ldots \\ dm_n'' &= -\delta m_n, \; dm_n' = \delta m_n, \end{aligned}$$

and hence

$$\begin{aligned} -\delta w &= \mu_1'\delta m_1 + \mu_2'\delta m_2 + \ldots + \mu_n'\delta m_n \\ &\quad - \mu_1''\delta m_1 - \mu_2''\delta m_2 - \ldots - \mu_n''\delta m_n \\ &= (\mu_1' - \mu'')\delta m_1 + (\mu_2' - \mu_2'')\delta m_2 + \ldots + (\mu_n' - \mu_n'')\delta m_n. \end{aligned}$$

The condition for equilibrium is therefore

$$(\mu_1' - \mu_1'')\delta m_1 + (\mu_2' - \mu_2'')\delta m_2 + \ldots + (\mu_n' - \mu_n'')\delta m_n \geqq 0. \quad \ldots\ldots(11)$$

This condition must hold for all positive and negative values which we may choose to assign to the variations $\delta m_1, \delta m_2, \ldots \delta m_n$, and this is only the case when

$$\begin{aligned} \mu_1' &= \mu_1'', \\ \mu_2' &= \mu_2'', \\ &\ldots\ldots\ldots \\ \mu_n' &= \mu_n''. \end{aligned}$$

It is now easy to prove that if we add a third solution C, furnished also with a thermostat at temperature T and a pressure regulator at pressure p, and containing the masses m_1''', m_2''', m_3''', $\ldots m_n'''$ of the same components, the isolated system

composed of all three solutions with their thermostats and pressure regulators is in equilibrium when

$$\mu_1' = \mu_1'' = \mu_1''',$$
$$\mu_2' = \mu_2'' = \mu_2''',$$
$$\cdots\cdots\cdots\cdots$$
$$\mu_n' = \mu_n'' = \mu_n'''.$$

For if the isolated system $A+C$ is in equilibrium we shall have

$$\mu_1' = \mu_1''',$$
$$\mu_2' = \mu_2''',$$
$$\cdots\cdots\cdots$$
$$\mu_n' = \mu_n''';$$

and since $A+B$ are in equilibrium

$$\mu_1' = \mu_1'',$$
$$\mu_2' = \mu_2'',$$
$$\cdots\cdots\cdots$$
$$\mu_n' = \mu_n'';$$

and hence

$$\mu_1'' = \mu_1''',$$
$$\mu_2'' = \mu_2''',$$
$$\cdots\cdots\cdots$$
$$\mu_n'' = \mu_n''';$$

so that the isolated system $B+C$ must also be in equilibrium. Hence the isolated system $A+B+C$ must be in equilibrium since there is no way in which work can be done in the transference of a small amount δm of any of the components from any part of the system to any other. The same line of reasoning may be extended to any number of solutions.

A system composed of r solutions with n components is therefore in equilibrium when the potential of each component is constant throughout the r solutions.*

8. Relationships between the thermodynamic functions. The Gibbs-Helmholtz equations.

In the preceding sections we have considered systems under various types of constraint and have been led to define for

* This relationship was discovered by Willard Gibbs (*Trans. Connecticut Acad. III.*, p. 108, 1875-76). His papers which are classical in thermodynamics have been published in book form, and are recommended to all who intend to study seriously in this field. (*The Scientific Papers of Willard Gibbs*, Longmans, Green and Co., London, 1906.)

several of these types a function of the variables of state having the property that the difference between the values of the function in two possible states of the constrained system is equal to what we may call the "effective" or available work. The available work is, for all types of constraint, the excess of the maximum work which the system does when the change of state is carried out reversibly, over the minimum work, *i.e.* the work done on the thermostats, pressure regulators, etc., which the system must do in virtue of the constraints even when the change of state takes place irreversibly. These functions, however, have a definite significance for every state of the system, apart altogether from the constraints which we choose to impose on its variation. Thus, for one and the same system in a given state, its total energy U, entropy S, heat content H, free energy Ψ and thermodynamic potential ζ have each a perfectly definite value. This is what we mean when we say that U, S, H, Ψ and ζ are functions of the variables of state alone and that dU, dS, dH, $d\Psi$ and $d\zeta$ are complete differentials. These functions must therefore be related to one another by definite equations, since all are expressible in terms of the same variables. Thus, for example, we have for a mol of a perfect gas

$$
\begin{aligned}
U &= c_v T + U_1, \\
S &= c_v lnT + Rlnv + S_1, \\
H &= U + pv = c_v T + pv + U_1, \\
\psi &= U - TS = c_v T - c_v TlnT - RTlnv - TS_1 + U_1, \\
\zeta &= \Psi + pv = c_v T - c_v TlnT - RTlnv - TS_1 + pv + U_1.
\end{aligned}
$$

We have expressed the five functions for a perfect gas in terms of the three variables p, v and T * but since these are connected by the equation $pv = RT$ we can eliminate any one of them and obtain expressions for each of the functions in terms of any two of the variables p, v and T. Our choice of independent variables is not, however, limited to p, v and T. Thus, for example, we

* The integration constants U_1 and S_1 are characteristic of the chemical nature of the gas. In pure thermodynamics we are concerned only with differences between the values of the functions in two states of the gas, so that we may omit the constants without affecting the results of our calculations.

may express the five functions in the above equations in terms of any pair of the variables p, v, T and S.*

Let us now consider a homogeneous system whose state is determined by the $n+2$ variables p, T, m_1, m_2, ... m_n. Its thermodynamic potential ζ is a function of these variables alone, and hence, by the rules of the differential calculus,

$$d\zeta = \frac{\partial \zeta}{\partial T} dT + \frac{\partial \zeta}{\partial p} dp + \frac{\partial \zeta}{\partial m_1} dm_1 + \ldots + \frac{\partial \zeta}{\partial m_n} dm_n$$
$$= \frac{\partial \zeta}{\partial T} dT + \frac{\partial \zeta}{\partial p} dp + \mu_1 dm_1 + \ldots + \mu_n dm_n.$$

If the composition of the system is kept constant we have

$$\delta\zeta = \frac{\partial \zeta}{\partial T} \delta T + \frac{\partial \zeta}{\partial p} \delta p.$$

We can, however, obtain another expression for $\delta\zeta$. Keeping the composition of the system constant as before, we have by the first law

$$\delta U = T\delta S - p\delta v,$$

and hence, by the definition of ζ,

$$\delta\zeta = \delta(U - TS + pv) = \delta U - T\delta S - S\delta T + p\delta v + v\delta p$$
$$= -S\delta T + v\delta p.$$

Comparing these two expressions for $\delta\zeta$, we see that

$$\frac{\partial \zeta}{\partial T} = -S \quad \text{and} \quad \frac{\partial \zeta}{\partial p} = +v. \qquad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Substituting these values in the complete expression for $d\zeta$ we have

$$d\zeta = -SdT + vdp + \mu_1 dm_1 + \ldots + \mu_n dm_n. \qquad \ldots\ldots\ldots (13)$$

Adding $d(TS) - d(pv)$ to both sides of this equation we obtain the expression for dU, namely,

$$dU = d(\zeta + TS - pv)$$
$$= TdS - pdv + \mu_1 dm_1 + \ldots + \mu_n dm_n. \qquad \ldots\ldots\ldots\ldots (14)$$

The total energy of the system is completely determined by its state, and hence U is a function of the variables p, T, m, ... m_n. But the state of the system (as we have seen in the case of a perfect gas) may be equally well stated in terms of the variables S, v,

* Since we have 6 equations between the 8 variables U, S, H, ψ, ζ, p, T, v, we can express any six of them in terms of the remaining two.

$m_1, \ldots m_n$, and hence U may also be expressed in terms of these variables alone. Hence, by the rules of the differential calculus,

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial v} dv + \frac{\partial U}{\partial m_1} dm_1 + \ldots + \frac{\partial U}{\partial m_n} dm_n.$$

Comparing these two expressions for dU we see that

$$T = \frac{\partial U}{\partial S}; \quad -p = \frac{\partial U}{\partial v}; \quad \mu_1 = \frac{\partial U}{\partial m_1}; \quad \ldots \mu_n = \frac{\partial U}{\partial m_n}. \quad \ldots\ldots(15)$$

We can obtain similar expressions for dH and $d\psi$. Thus, subtracting $d(TS) = TdS + SdT$ from both sides of equation (14), we obtain

$$d\psi = d(U - TS)$$
$$= -SdT - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n. \quad \ldots\ldots(16)$$

Since the state of the system is determined when the variables $T, v, m_1, m_2, \ldots m_n$ are given, the free energy ψ can be expressed as a function of these variables alone. Hence, by the same reasoning as before,

$$-S = \frac{\partial \psi}{\partial T}; \quad -p = \frac{\partial \psi}{\partial v}; \quad \mu_1 = \frac{\partial \psi}{\partial m_1}; \quad \ldots \mu_n = \frac{\partial \psi}{\partial m_n}. \quad \ldots\ldots(17)$$

Similarly, by subtracting $d(pv) = pdv + vdp$ from equation (14) we obtain

$$dH = TdS + vdp + \mu_1 dm_1 + \ldots + \mu_n dm_n. \quad \ldots\ldots\ldots\ldots(18)$$

Hence $$T = \frac{\partial H}{\partial S}; \quad v = \frac{\partial H}{\partial p}; \quad \mu_1 = \frac{\partial H}{\partial m_1}; \quad \ldots \mu_n = \frac{\partial H}{\partial m_n}. \quad \ldots\ldots\ldots(19)$$

The chemical potential μ_1 may therefore be defined by any of the equations

$$\mu_1 = \left(\frac{\partial \xi}{\partial m_1}\right)_{p, T, m_2, \ldots m_n} = \left(\frac{\partial U}{\partial m_1}\right)_{S, v, m_2, \ldots m_n}$$
$$= \left(\frac{\partial \psi}{\partial m_1}\right)_{T, v, m_2, \ldots m_n} = \left(\frac{\partial H}{\partial m_1}\right)_{S, p, m_2, \ldots m_n}, \quad \ldots\ldots\ldots(20)$$

with similar equations for the other potentials.

The Gibbs-Helmholtz equations. For a homogeneous system whose state is determined by the variables $p, T, m, \ldots m_n$ we have by equation (12)

$$\left(\frac{\partial \xi}{\partial T}\right)_{p, m_1, \ldots m_n} = -S,$$

and hence, by the definition of ζ,

$$\zeta = H - TS,$$

or

$$\zeta = H - T\left(\frac{\partial \zeta}{\partial T}\right)_{p, m_1, \ldots m_n} \quad \ldots\ldots\ldots\ldots\ldots\ldots (21)$$

Again, since the state of the system may also be expressed in terms of T, v, $m_1, \ldots m_n$, we have, by (17),

$$\left(\frac{\partial \psi}{\partial T}\right)_{v, m_1, \ldots m_n} = -S,$$

and hence

$$\psi = U - TS,$$

or

$$\psi = U - T\left(\frac{\partial \psi}{\partial T}\right)_{v, m_1, \ldots m_n} \quad \ldots\ldots\ldots\ldots\ldots\ldots (22)$$

These equations are of great importance in chemistry and physics. They were first derived by Helmholtz and independently by Willard Gibbs in connection with the theory of galvanic cells. The former of the two equations is the more generally useful in chemistry, since it is easier as a rule to keep the pressure on a system constant than to maintain it at constant volume. We shall have frequent examples of the application of equation (21) in the subsequent chapters of this book.

CHAPTER VII.

GENERAL DEDUCTIONS FROM THE TWO LAWS OF THERMODYNAMICS.

1. The phase rule.

A homogeneous chemical substance, for example an element such as sulphur or a compound such as water, may exist in several, and must be capable of existing in at least three different forms, viz. as gas, as liquid, and as solid. In many cases the solid may exist in various allotropic modifications, which differ from one another in crystalline form, melting point, density, specific heat, and, in fact, in all their physical properties. Every portion of matter which is in itself homogeneous, *i.e.* in which the smallest visible particles are exactly alike, and which is therefore separated in space from every other homogeneous but dissimilar portion of matter, was called by Willard Gibbs a "phase."

We shall now investigate the conditions under which different phases of the same substance, *e.g.* ice with liquid water and with water vapour, are in equilibrium with one another.

For each phase we have one equation of condition, or, in other words, the three variables, pressure, temperature, and volume, which determine completely the condition of a system not under the influence of electrical, magnetic, or other forces, are not independent of one another. If we fix two of these variables arbitrarily, the third is determined by an equation of the form

$$F(T, p, v) = 0.$$

In future the symbol v will be taken to mean the volume of unit mass of the substance. If we take 1 gr. as unit mass of

the substance, v is the specific volume. If we take 1 mol. (the molecular weight in grams) as unit of mass, then v is the molecular volume. In many cases it is convenient to take the concentration (mass per unit of volume) $c = \frac{1}{v}$ as variable of condition instead of v. The equation of condition then assumes the form

$$F(T, p, c) = 0.$$

We can show in two ways that an equation of condition of this form must exist for each homogeneous phase. In the first place, we know by experience that an alteration of any of the three variables always produces a change in the other two. In the second place, it follows from the statistical theory of nature that of all possible arrangements of the molecules and their velocities, only one can have the greatest probability, and hence be the stable arrangement. In the previous chapter we showed how the equation of condition of a perfect gas could be deduced in this way. If we knew the nature of the molecular motion, and the forces acting between the molecules, we could deduce the equation of condition in a similar manner for any phase.*

Thus experience and theory both lead to the same conclusion, that each phase must have an equation of condition characteristic of it alone.†

Let us first consider a single phase. It will always assume the state corresponding to stable equilibrium. Even if two of the variables of condition are chosen arbitrarily, the third variable will assume of its own accord the value which satisfies the equation of condition. The number of variables which can be altered at will consistently with the possibility of stable equilibrium is called the number of degrees of freedom of the system. A single isolated phase has therefore two degrees of freedom.

If we have two phases of one and the same substance in equilibrium with one another, *e.g.* water and vapour or ice and water, the two phases can differ from one another only in the value

* See Gibbs, *Statistical Mechanics*; P. Hertz, *Ann. d. Physik* (4), **33**, 225, 1910.

† The necessity for the existence of an equation of condition cannot be deduced from the two laws of thermodynamics alone (see also A. Byk, *Ann. d. Phys.* **19**, 441, 1906).

of v (or c), since they are in equilibrium only when temperature and pressure are the same in both phases. Let the values of c in the two phases be c_1 and c_2. We have then two equations

$$F_1(T, p, c_1) = 0 \text{ for the first}$$

and

$$F_2(T, p, c_2) = 0 \text{ for the second phase.}$$

Each of these equations is consistent with an indefinite number of states of the two phases. The condition that they shall be in equilibrium with one another must therefore be expressed by a third equation.

It was shown in Chapter V. that the isothermal transformation of unit mass of a substance from one phase to another is reversible when the two phases are in equilibrium with one another. The change in entropy during this isothermal process is therefore

$$S_1 - S_2 = \frac{Q}{T},$$

where Q is the quantity of heat necessary to bring about the change of phase. As S_1 is a function of T, p, and c_1, and S_2 of T, p, and c_2, and as Q is a quantity depending on the chemical nature of the substance and on the variables of condition of the two phases in equilibrium, the above equation gives us a third equation connecting the four variables (T, p, c_1, c_2), which we may write in the form

$$F_3(T, p, c_1, c_2) = 0.$$

We can derive this equation in another way. There will be equilibrium between the two phases (at constant temperature and pressure) when the "chemical potential" of the substance has the same value in both phases (see p. 178). As the "chemical potential" μ, like the entropy, is a function of the variables of condition, it follows that

$$\mu_1(p, T, c_1) = \mu_2(p, T, c_2).$$

There are, therefore, three equations which must be satisfied by the four variables of condition, T, p, c_1, and c_2, so that only one of them can be chosen arbitrarily.

A system consisting of one substance in two coexistent phases has therefore only one degree of freedom.

Applying this result to the equilibrium between a liquid and its vapour, we arrive at the familiar experimental fact, that if we fix the temperature arbitrarily, the vapour pressure, and hence also the specific volumes of the liquid and of the saturated vapour assume definite values independent of the quantity of the two phases.

For the equilibrium liquid-solid it is usual to choose the pressure as the sole independent variable. In this way the melting point is fixed as the one temperature at which the solid and the liquid phase are in equilibrium with one another at a given pressure.

Equilibrium between three phases. If three phases of the same substance are in equilibrium with one another, the equations of condition must be satisfied for all three phases, viz.

$$F_1(T, p, c_1) = 0,$$
$$F_2(T, p, c_2) = 0,$$
$$F_3(T, p, c_3) = 0.$$

Further, since all three phases are in equilibrium with one another, we have the following two equations for the change in entropy corresponding to the change from one phase to another:

$$S_1 - S_2 = \frac{Q}{T},$$

$$S_2 - S_3 = \frac{Q'}{T},$$

or

$$\mu_1 = \mu_2 = \mu_3.$$

We have thus five equations to determine the five quantities T, p, c_1, c_2, and c_3, and hence no degrees of freedom. Three phases in presence of one another are stable at only one temperature and one pressure. At any other temperature or pressure one phase vanishes, *i.e.* is converted into the other two. The point in the p, T diagram corresponding to these singular values of p and T is called the "triple point" of the system.

The coexistence of a fourth phase in equilibrium with the other three, *e.g.* another modification of ice (ice II. or ice III.), would introduce two new equations besides the five above, namely, $F_4(T, p, c_4) = 0$ and $\mu_4(T, p, c_4) = \mu_1(T, p, c_1)$. As the functions F_4 and μ_4 must necessarily be different from the others,

these conditions can never all be satisfied. A single substance can therefore be obtained in at most three coexistent phases. Designating the number of coexistent phases by P and the degrees of freedom by f, we have, for a single substance,

$$P+f=3.$$

Fig. 20 is a graphical representation of the above relationships (T as abscissae and p as ordinates). The regions in which a single phase (two degrees of freedom) is stable are the three portions into which the p, T plane is divided. Each of the curves separating any two of these regions corresponds to the coexistence of two phases (liquid-gas, solid-gas, and solid-liquid, each with 1 degree of freedom).

The triple point O at which all three phases are in equilibrium is the common intersection of the three boundary curves.

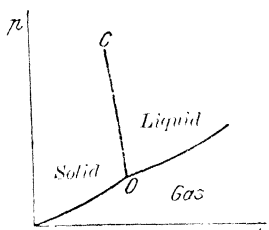


FIG. 20.

We see at once from the figure that we can have equilibrium between the liquid and the solid phase for a continuous series of temperatures. The melting point of a solid, like the boiling point of a liquid, is dependent on the pressure at which the change of phase takes place. The variation of the melting point with pressure, unlike that of the boiling point, is generally so slight that we may neglect it in practice. For this reason the triple point, often called the true melting point, generally differs very slightly from the melting point determined at atmospheric pressure. For water the difference is only 0.0074°.

A single substance which can exist in two or more solid modifications has therefore several triple points, the maximum number of which can be computed by the law of combinations. Thus for sulphur, which can exist in two crystalline forms (rhombic and monoclinic), we have the following triple points:

1. Rhombic sulphur, liquid, and vapour.
2. Monoclinic sulphur, liquid, and vapour.
3. Rhombic sulphur, monoclinic sulphur, and liquid.
4. Rhombic sulphur, monoclinic sulphur, and vapour.

Each of these four points corresponds to definite values of T and P. It is not, however, always possible to realise all these points experimentally. Thus, if a triple point occurred in the region of the fourth phase with which the other three are not in equilibrium, it could have no real existence.

The equilibrium curves for the various modifications of sulphur are shown in Fig. 21. *rd* is the curve for rhombic sulphur-gas, *md* for monoclinic sulphur-gas, and *fd* for liquid-gas. The modification which has the lowest vapour pressure is the most stable modification, and always forms at the expense of those which have a higher vapour pressure. The four intersections of each

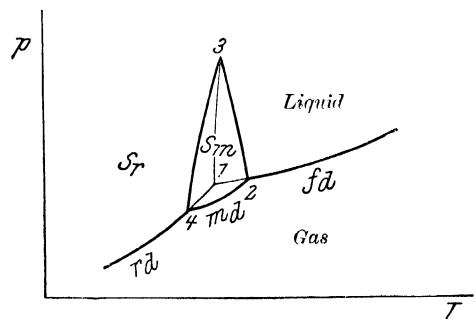


FIG. 21.

pair of curves are the triple points 1, 2, 3, and 4 enumerated above. 1 is the true melting point of rhombic sulphur, *i.e.* the melting point at the pressure of the saturated vapour. 2 is the true melting point of monoclinic sulphur, and 4 is the transition point of the two modifications. Above 96° monoclinic sulphur is more stable than rhombic sulphur, so that the true melting point of rhombic sulphur occurs in a region in which it is unstable.

The possibility of determining this point experimentally is dependent on the rate at which rhombic sulphur changes into monoclinic sulphur above 100°. We know experimentally that the velocity of transition is so small that the melting point of rhombic sulphur can be determined without difficulty. The curves 3 4, 3 1, and 3 2 (obtained in part by extrapolation) show the variation of the transition temperature and of the two melting points with pressure. All three curves must inter-

sect in one point, as rhombic and monoclinic sulphur must be in equilibrium with one another when both are in equilibrium with the liquid phase. This common point of intersection is the triple point 3.

Water is an example of a substance which can exist in five different phases. It has been obtained in three solid modifications. The p, T diagram of water has been very accurately determined recently by Tammann.

Two component systems. Let us now consider systems of two component substances which can react with one another. The reaction may consist of the formation of solutions, or of one or more chemical compounds. By solutions we mean phases which contain both components, and which remain homogeneous when their percentage composition is varied continuously within certain limits. As each component of the system and each compound of the components can exist in at least three modifications, it would at first sight appear possible for a great number of such phases to exist in equilibrium with one another. We shall see, however, that the number of phases which can exist in contact with one another is limited in various ways.

In the first instance, it follows from the previous chapter (p. 146) that different gases in contact with one another can never remain separate, and that equilibrium between the gases can only be established when each gas is uniformly distributed throughout the whole of the available space. In other words, there will not be equilibrium until the whole of the gaseous space is filled with a single homogeneous phase. Liquid phases in general are stable in contact with one another, but many liquids, like gases, are miscible in all proportions. Water-ether and water-benzene are examples of the first, and water-alcohol of the second type. In a reaction between solids and liquids it will rarely be possible for many liquid phases to exist in equilibrium with one another, as the range of temperature in which a liquid can exist at all (between the melting point and the critical point) is limited for each substance. In a system consisting of a salt and water, the melting point of the salt will often be above the critical temperature of water, and thus the coexistence of liquid-water and molten salt will be impossible.

In certain cases different solids form homogeneous phases with one another, so-called solid solutions. This also has the effect of reducing the number of phases which can exist in equilibrium with one another.

Apart from these considerations, the number of phases is limited in a quantitative manner by thermodynamics. If we assume, in the first instance, that the two component substances form only two phases with one another, we have for these two phases two equations of condition of the form

$$F_1(p, T, c_1, c_1') = 0, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$F_2(p, T, c_2, c_2') = 0, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where the concentrations of the first component in the two phases are c_1 and c_2, and those of the second component c_1' and c_2'. The state of a phase containing both components is now determined by four quantities, the temperature, the pressure, and the two concentrations, in such a manner that if three of these four quantities are fixed arbitrarily, the fourth is uniquely determined. A homogeneous phase containing two components has therefore three degrees of freedom. If the two phases are in equilibrium with one another, the potential of each component in one phase must be equal to its potential in the other phase. We have thus two further equations :

$$\mu_1(p, T, c_1) = \mu_2(p, T, c_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

and

$$\mu_1'(p, T, c_1') = \mu_2'(p, T, c_2'). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The six variables p, T, c_1, c_2, c_1', c_2', are therefore connected by four equations, so that only two of them can be chosen at will. The system has therefore two degrees of freedom.

We arrive at the same conclusion if we assume that one of the two components is present in one phase only, as is often the case in practice, for example in the equilibrium, salt solution —water vapour. Here the concentration of the salt in the gaseous phase is practically zero. Thus the variable c_2' disappears, but so also does equation (4), as the only process consistent with the nature of the system is the transfer of one component (water) from the one phase to the other. Here again there are $5-3=2$ degrees of freedom.

The meaning of this statement is as follows: In the example (equilibrium between salt solution and water vapour) two quantities can be chosen at will, *e.g.* the temperature and the concentration of the salt in the solution. The vapour pressure of the solution is then determined, and is independent of the quantity of the solution. In other words, at a given temperature and pressure, water vapour is in equilibrium with a solution of one definite concentration only.

If three phases are in equilibrium with one another, we have three equations of condition:

$$F_1(p, T, c_1, c_1') = 0,$$
$$F_2(p, T, c_2, c_2') = 0,$$
$$F_3(p, T, c_3, c_3') = 0,$$

and four equations for the potentials of the two components:

$$\mu_1(p, T, c_1) = \mu_2(p, T, c_2) = \mu_3(p, T, c_3),$$
$$\mu_1'(p, T, c_1') = \mu_2'(p, T, c_2') = \mu_3'(p, T, c_3'),$$

in all seven equations for the eight variables p, T, c_1, c_2, c_3, c_1', c_2', c_3'. Hence only one variable can be chosen arbitrarily, and the system has only one degree of freedom. If either of the components is absent in one or more of the three phases (as in the previous example), the number of variables is reduced, but the number of equilibrium conditions is reduced correspondingly, so that the system has still one degree of freedom.

Applying these results to the system water-salt, we see that when salt solution and water vapour are in equilibrium the temperature only can be varied at will, and that if we fix the temperature, the concentration of the solution (solubility) and the vapour pressure of the saturated solution are determined.

If four phases are in equilibrium with one another, the number of variables is increased by two, viz. the concentrations of the components in the fourth phase. The number of equations, on the other hand, is increased by three, viz. the equation of condition of the fourth phase and the equilibrium conditions governing the transfer of the two components into any other

phase. There are now as many equations as there are variables, so that the system has no degrees of freedom, and can only exist at a single temperature and pressure. Solid salt, ice, saturated solution, and water vapour are in equilibrium only at the "cryohydrate" temperature and the pressure corresponding to the vapour pressure of ice at this temperature. A point of this kind in the pT diagram is called a quadruple point.

Summarising these results, we have for the relationship between the number of phases and the degrees of freedom of a two component system the equation

$$P+f=4.$$

In a similar manner we can calculate the degrees of freedom for a system of n components and P phases.

For the P phases we have P equations of condition of the form $F(T, p, c, c', c'' \ldots c^{n'})=0$. Each of the n components must also satisfy $P-1$ equilibrium conditions of the form

$$\mu_1(T, p, c_1)=\mu_2(T, p, c_2)=\mu_3(T, p, c_3)=\ldots=\mu_P(T, p, c_P).$$

We have, therefore, $n(P-1)$ equilibrium conditions and in all $n(P-1)+P$ equations. The number of variables is $nP+2$, as each component can be present in P phases, and pressure and temperature are also variable. The degrees of freedom are therefore given by

$$f=nP+2-[n(P-1)-P]=n+2-P*$$

or

$$P+f=n+2.$$

This relationship was first discovered by Willard Gibbs, and is known as the phase rule.

The number of independent components n, which take part in the equilibrium, must be defined more closely than we have done as yet. n is not the number of chemical compounds in the system, but is the number of different molecular species not connected with one another by a chemical equation. Each

* If one or more components are absent in any of the phases, the reduction in the number of variables is equal to the reduction in the number of the equilibrium conditions, so that the degrees of freedom are unaltered.

chemical equation is a new relationship between the variables, and the components involved in the equation are not independent.

In complicated cases the number of independent components can be obtained most easily as follows: add together all the molecular species which take part in the equilibrium, and subtract the number of chemical equations which come into play when the system is displaced from equilibrium. Nernst's definition of the number of independent components is equivalent to this. According to Nernst, n is the minimum number of molecular species which is sufficient to build up all the phases of the system.*

If two different solid phases have the same density at all temperatures at which they are capable of existing, they must have the same equation of condition $F(T, p, v)=0$. Nevertheless, they need not be identical, but may differ in crystalline form. We meet with this case in enantiomorph forms of optically active solids, which rotate the plane of polarisation of light in opposite directions. If two phases of this kind take part in an equilibrium, the number of equations is reduced by one, and is therefore $(n+1)(P-1)$. In this case the phase rule is

$$P+f=n+3.$$

For the same number of degrees of freedom, the number of phases which take part in the equilibrium is greater by one than in ordinary cases. In other words, two enantiomorph optically active substances behave thermodynamically as if they belonged to the same phase. From this it necessarily follows that enantiomorph substances must have the same vapour pressure, the same solubility, and the same melting point.

A few examples will illustrate the application of the phase rule to chemical equilibria. Systems consisting of the various phases of a single component substance have already been discussed in the beginning of the chapter. We shall now consider systems with two independent components. An example of this kind is the system calcium chloride and water. We know by

* *Lehrbuch*, 6th edition, p. 608.

experiment that the following phases can be obtained from these two substances :

1. The gaseous phase consisting of water vapour.
2. A liquid phase consisting of a solution of $CaCl_2$ in H_2O, or of water in molten $CaCl_2$, or in a molten hydrate.
3. Solid H_2O (ice).
4. Solid $CaCl_2$.
5-9. Solid compounds of $CaCl_2$ and H_2O, viz. salts with water of crystallisation.

According to Roozeboom, the following compounds are known in the solid state : $CaCl_2$, $6H_2O$; $CaCl_2$, $4H_2O\alpha$; $CaCl_2$, $4H_2O\beta$; $CaCl_2$, $2H_2O$; $CaCl_2$, H_2O.

Of these nine phases only $2+2=4$ can exist at any one time in contact with one another, and these only at quite definite temperatures and pressures. If we have a complete equilibrium of this kind and change the temperature, one of the four phases must disappear and be converted into one or more of the others.

The temperatures and pressures of those quadruple points, in which two of the four phases consist of vapour and saturated solution are tabulated below along with the corresponding solid phases : *

$t°$	p mm. Hg.	Solid phase.	
−55	very small	ice	$CaCl_2$, $6H_2O$
+29·2	5·67	$CaCl_2$, $6H_2O$	$CaCl_2$, $4H_2O\beta$
+29·8	6·80	$CaCl_2$, $6H_2O$	$CaCl_2$, $4H_2O\alpha$
+38·4	7·88	$CaCl_2$, $4H_2O\beta$	$CaCl_2$, $2H_2O$
+45·3	11·77	$CaCl_2$, $4H_2O\alpha$	$CaCl_2$, $2H_2O$
175·5	842	$CaCl_2$, $2H_2O$	$CaCl_2$, H_2O
circa 260	several atmospheres	$CaCl_2$, H_2O	$CaCl_2$

Let us now consider the systems which have one degree of freedom (so-called monovariant systems). According to the phase rule, these must consist of three phases, and may contain : gas, solution, and solid phase, or gas and two solid phases. Systems composed of solid phases alone, or of solid and liquid phases alone, are called condensed systems. Condensed systems

* See Abegg, *Handb. d. anorg. Chemie*, vol. ii. p. 95.

can only exist at pressures which are greater than the vapour pressure of the solution or the dissociation pressure of the solid substances. They are therefore difficult to investigate, and the determinations have been carried out only in a few cases. In the meantime, we shall not consider condensed systems.

The concentration and the vapour pressure of the solution have a definite value for each temperature. Plotting the concentrations of the saturated solutions against the temperatures, we obtain the "solubility curves" of the various solid phases which are in equilibrium with the saturated solution.

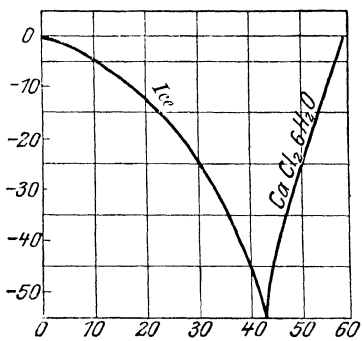


FIG. 22*a*.

Each hydrate has a definite solubility curve. At the intersection of the solubility curves of two different solid phases, the solution is saturated with respect to both phases. These intersections appear as discontinuities in the slope of the total solubility curve, and are the quadruple points tabulated above.

On either side of a quadruple point the solution is supersaturated with respect to one of the solid phases, which would therefore change in contact with the solution into the hydrate of lower solubility. The quadruple point is therefore also called the transition point of the two hydrates. In Fig. 22 the solubility curves of the various hydrates of calcium chloride (*a*, *b*, and *c*) are plotted for temperatures up to 260°. The formulae of the solid phases are written opposite the corresponding curves.

In Fig. 22*a* the downward curve corresponds to the freezing points of $CaCl_2$ solutions at varying concentrations (saturation with respect to ice). The middle portion of the curve in

Fig. 22*b* shows that the hydrate α is unstable with respect to the tetrahydrate β throughout the whole range of temperature in which it can exist at all. The tetrahydrate β has always the lower solubility of the two. The preparation of the tetrahydrate α and the determination of its solubility are only possible owing to the slowness of the transition into the stable hydrate.

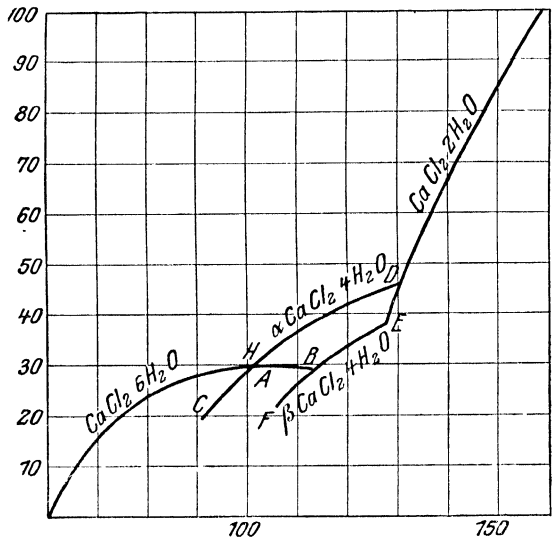


FIG. 22*b*.

Systems consisting of two different hydrates and vapour have a definite vapour pressure at every temperature. The vapour pressure of the solution, which is a measure of the tendency of the hydrate to give up water, is not completely defined unless the compound (containing less water) which results on the dissociation of the hydrate is also specified. The corresponding pressure temperature diagrams, *i.e.* the vapour pressure curves, also intersect at quadruple points, namely, those at which three solid phases are in equilibrium with water vapour, *e.g.* ice, hexahydrate, and tetrahydrate β, or hexahydrate, tetrahydrate β and dihydrate.

These quadruple points correspond to really stable equilibria only when their vapour pressure is less than the vapour pressure of the saturated solution of each hydrate. Otherwise the water

vapour and the highest hydrate must unite to form solution. For calcium chloride this is always the case. So far, an equilibrium between three different solid phases has never been observed.

The state of a system with two phases, and hence two degrees of freedom (divariant system), is not determined until two of its variables have been arbitrarily specified. The most important case is the coexistence of water vapour with a solution of calcium chloride. Here temperature and concentration determine the vapour pressure. Hence the vapour pressure of the solution at constant temperature is a function of its concentration. From this again it follows that the vapour pressure of a solution is always different from the vapour pressure of the pure solvent at the same temperature.

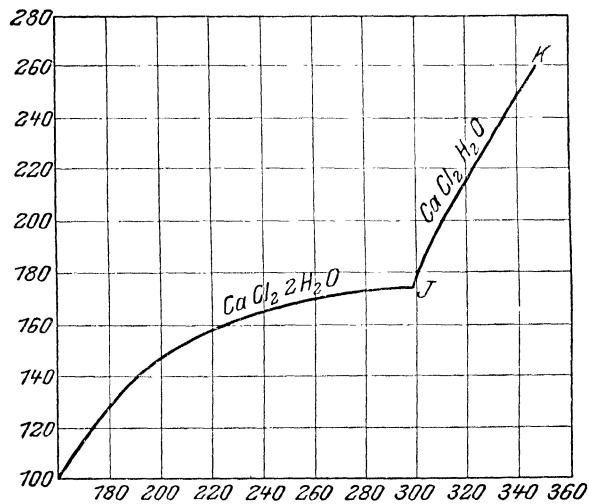


FIG. 22c.

The relationship between the vapour pressure and the concentration cannot, however, be deduced from thermodynamics alone.

Other important examples of two component systems are the heterogeneous dissociation equilibria, in which a chemical compound in one phase forms products of decomposition which belong to a different phase. The standard example of a reaction of this kind is the decomposition of calcium carbonate according to the equation $CaCO_3 = CaO + CO_2$. Here we have three com-

ponents connected by one chemical equation, and hence two independent components and three phases, namely, $CaCO_3$ (solid), CaO (solid), and CO_2 (gas). The system has therefore one degree of freedom, and every temperature corresponds to a definite dissociation pressure, which is given in the following table:

$t°$ C.	p (mm.).	$t°$ C.	p (mm.).
605	2·3	840	311
608	15·8	881	603
727	44	894	716
786	134	—	—

The technical decomposition of limestone (burning of lime to quicklime) can be carried to completion either by raising the temperature until the dissociation pressure is higher than the atmospheric pressure, so that the CO_2 can escape, or by removing the CO_2 as it is formed by means of a current of inert gas, so that the partial pressure of the CO_2 is always less than the dissociation pressure. Thus the burning of lime is facilitated by blowing in steam or carbon monoxide.

In the decomposition of ammonium chloride, according to the equation $NH_4Cl = NH_3 + HCl$, we have only two phases, solid and gaseous. The dissociation pressure, therefore, is not determined until we have fixed another variable besides the temperature, *e.g.* the concentration of either of the gaseous products of decomposition. We have then determined not only the total pressure, but also the partial pressure and concentration of the other product of decomposition.

We see, therefore, that the concentrations of gases which are in chemical equilibrium with one another, and with a solid substance, are not independent, but must be connected by some relationship. We cannot, however, deduce the nature of this relationship without introducing fresh assumptions. This is another case in which thermodynamics has to be supplemented by extraneous hypotheses.

When solid ammonium chloride is heated in vacuo or in an atmosphere of an inert gas, a definite equilibrium pressure is reached at each temperature, in apparent contradiction with

what has just been stated. The system has apparently only one degree of freedom. Under these conditions, however, we have in reality fixed a second variable, namely, the ratio of the concentrations of the products of decomposition NH_3 and HCl, which must always remain in equivalent proportions. Ammonium chloride and its vapour are therefore in a certain sense a one-component system, as we can build up any state of the system from the one molecular type NH_4Cl.

In some dissociations the solid components may form solid solutions with one another, *e.g.* the dissociation of copper oxide according to the equation $2CuO = Cu_2O + \frac{1}{2}O_2$. According to Wöhler and Foss,* the dissociation pressure is not solely determined by the temperature, but diminishes if the dissociation is pushed further by pumping out the oxygen formed. The cause of this variation in the pressure at constant temperature is the formation of a homogeneous solid solution of cuprous in cupric oxide. We have, therefore, only two phases (solid solution and gas), and hence two degrees of freedom (temperature and concentration of the solid phase).†

Further examples. Three independent components. Consider a system composed of water and two soluble salts which have a common ion, and which form a double salt, *e.g.* magnesium chloride and potassium chloride. These two salts can combine according to the equation $MgCl_2 + 2KCl = MgCl_2 . 2KCl$ (carnallite). We have thus four different types of molecules and one chemical equation connecting them, hence three independent components. The maximum number of coexistent phases is therefore five, *e.g.* the three solid salts, saturated solution, and water vapour. The coexistence of these phases is, however, only possible at one temperature, namely, the transition temperature of the double salt.

At all other temperatures the solution can only be saturated with respect to two salts, viz. the two simple salts, or one of the simple salts and the double salt. The concentration of the solution and the vapour pressure are then determined by the

* *Zeitschr. f. Elektrochemie*, **12**. 781 (1906).

† See also the dissociation of potassium permanganate into manganite and oxygen (F. Bahr and O. Sackur, *Zeitschr. f. anorgan. Chemie*, **72**, 101, 1911).

temperature and by the nature of the two solid phases. At temperatures at which both simple salts are in equilibrium with solution, the double salt is always unstable, and breaks up in presence of the solution. The region of temperature in which this occurs may be above or below the transition point, according to the case under consideration. The phenomena may be still further complicated if one or both of the simple salts form solid hydrates.

When only one solid phase is present, the total concentration of the solution is indeterminate, and may be altered by addition of the other simple salt or of the double salt. The solubility of a salt is therefore not affected by the addition of a salt with a common ion. For the graphical representation of the equilibria in a three-component system, it is convenient to use a three-dimensional system of coordinates, of which the axes are the temperature and the concentrations of the two simple salts. Each point in the space corresponds to a definite vapour pressure. Monovariant equilibria are represented by lines, and bivariant equilibria by surfaces in the space model. (See van't Hoff, *Bildung und Spaltung von Doppelsalzen*, Leipzig 1897; also van't Hoff u. Meyerhoffer, *Zeitschr. f. physikal. Chemie*, **30**, 64 (1899), and others. Experimental methods of determining the transition point are also described there.)

Four independent components. Water and two salts which have no ion in common are an example of a four-component system, because the two salts can form a second pair of salts by double decomposition, according to the equation

$$\overset{1}{AB} + \overset{2}{CD} = \overset{3}{AD} + \overset{4}{BC},$$

e.g.

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Use is made of this double decomposition in the technical preparation of potassium nitrate from Chili saltpetre. Four salts connected by an equation of the above kind are called reciprocal pairs of salts. A further example of this kind is the manufacture of sodium bicarbonate by the Solvay process, viz.

$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

As the four salts (or their ions) are connected by one equation, there are only three independent components. Water is the

fourth component. Hence, by the phase rule, a solution of all four salts can only be saturated at a single temperature, again called the transition temperature. At all other temperatures only three solid phases can be in equilibrium with the saturated solution, *e.g.* 1, 2, and 3 in the above equation. Dissolving 4 in the solution causes an equivalent quantity of 3 to go into solution, while the corresponding quantities of 1 and 2 are precipitated, since the concentration of the solution must remain unaltered.

If the solution is saturated with respect to two salts only, we have besides the temperature one degree of freedom, *i.e.* the concentration of one of the salts in the solution. If only one salt is present, the concentrations of two salts can be fixed at will. If no solid phase is present, we have three degrees of freedom besides the temperature. From this we have the following consequences: In a dilute solution the concentrations of three salts can be specified at will. The concentration of the fourth salt is then determined. Thus, if the solution is prepared by dissolving three of the salts, double decomposition must take place until the concentration of the fourth has attained the equilibrium value. When the solution is evaporated at constant temperature, the concentrations of all the salts increase until finally the solution is saturated with respect to one of them. On further evaporation the least soluble salt must separate out, and double decomposition must take place until the pair of salts to which the least soluble salt belongs has disappeared at the expense of the reciprocal pair.

Equilibria in systems containing more than four independent components have hitherto rarely been investigated. The five-component system obtained on shaking up metallic tin with solutions of lead chloride in hydrochloric acid has been investigated by Sackur.* Here metallic lead is precipitated according to the equation $Sn + PbCl_2 = Pb + SnCl_2$.

These four atoms and molecules represent three independent components as they are connected by a chemical equation. The fourth and fifth components are water and hydrochloric acid. The solid phases of the system are lead, tin, and lead chloride;

* *Arbeiten aus d. Kaiserl. Gesundheitsamt*, **20**, 512 (1904); *Zeitschr. f. Elektrochemie*, **10**, 522 (1904).

the others, solution and vapour. There are, therefore, two degrees of freedom; the temperature and the concentration of the hydrochloric acid. In accord with theory it was found that at each HCl concentration the precipitation of lead by tin stopped when a definite percentage composition of $PbCl_2$ and $SnCl_2$ had been reached. If the solution is not saturated with respect to lead chloride so that the number of phases is reduced by one, the equilibrium concentration of $SnCl_2$ is indeterminate unless the concentration of the lead chloride is fixed arbitrarily.

2. The principle of Le Chatelier and Braun.

In chap. VI., p. 171, we showed that the heat of reaction Q_p at constant pressure is equal to the change during the reaction in the heat content H of the system. This follows from the equation

$$Q_p = (U_2 + pv_2) - (U_1 + pv_1) = H_2 - H_1.$$

If the change in volume at constant pressure is slight, so that $pv_2 - pv_1$ may be neglected, as is usually the case for reactions between solids and liquids, we have

$$Q_p = U_2 - U_1 = H_2 - H_1.$$

For reactions carried out at constant volume, we have

$$Q_v = U_2 - U_1,$$

where Q_v is the heat of reaction at constant volume.

The difference between Q_p and Q_v is most marked in the case of gas reactions involving a change in the number of molecules, since the change in volume of the reacting system is considerable under these circumstances.

Equation (1), however, is not restricted in application to chemical reactions, but may be applied to any change in a system involving absorption or emission of heat at constant pressure. The quantity Q_p is named differently according to the nature of the change. Thus it is called:

heat of evaporation	for the change	-	liquid-gas.
heat of sublimation	,, ,,	-	solid-gas.
heat of fusion	,, ,,	-	solid-liquid.
heat of solution	,, ,,	-	solute-solution.
heat of transition	,, ,,	-	solid-solid, etc.

We shall use the term latent heat L as a generic name for these different heats.

If the latent heat L is absorbed when any of the processes enumerated above takes place in a given direction, the same amount of heat L will be emitted when the process is reversed.

Consider a system consisting of a number of phases made up of several different components, and suppose that the number of variables and conditions of constraint is such that the system has one degree of freedom. If we assign in addition a value to any one of the variables which characterize the state of the system (such as temperature, pressure, or the concentration of one of the components in one of the phases) the system will come to a perfectly definite state of equilibrium. Such an equilibrium is called a monovariant equilibrium. Rooseboom, to whom many important investigations on the phase rule and its applications are due, used the term " complete equilibrium " for an equilibrium of this kind. Nernst also adopts this terminology, although he raises objections to it, since monovariant equilibria are in no way more complete than nonvariant or multivariant equilibria. It would be more appropriate to use the term complete equilibria for nonvariant equilibria in which the number of phases is a maximum. (See Nernst, *Lehrbuch*, 6th ed. p. 473.)

We now ask ourselves the question whether it is possible to determine the direction in which the equilibrium is displaced, by a change in the one variable (*e.g.* the temperature) which is still left arbitrary. The answer to this question was given by Le Chatelier* and nearly simultaneously by F. Braun.†

The increase in total energy of any system can always be written in the form.

$$dU = X_1 dx_1 + X_2 dx_2 + \ldots + X_n dx_n,$$

where $x_1, x_2, \ldots x_n$ are any set of variables by which the state of the system is determined. The quantities $X_1 \ldots X_n$ are called *intensity* factors, and the quantities $x_1, x_2, \ldots x_n$ *quantity* factors. Thus temperature may be regarded as the

* *Compt. rend.* **100**, 441 (1885).

† *Sitzb. kgl. bayr. Akad.* 3rd July, 1886. See also *Ann. d. Physik*, **32**, 1102 (1910).

intensity factor, and entropy as the quantity factor for a change in energy due to absorption of heat. Pressure and volume are intensity and quantity factors for a change in energy due to compression, and so on. If we increase any quantity factor, say x_r by dx_r, the corresponding change in the intensity factor X_r will depend in general on the manner in which the other quantity factors have altered.

The principle of Le Chatelier may now be stated as follows: If a system is in stable equilibrium the increase in the intensity factor X_r, corresponding to a given increase dx_r in the quantity factor x_r, is smaller for a change to another state of stable equilibrium than for a change produced by altering x_r by dx_r, while all the other quantity factors remain constant.

For example, if heat supplied to a system consisting of several phases and components (increase in entropy) causes the temperature to rise by T, the phases otherwise remaining unaltered, then the same amount of heat (increase in entropy) will raise the temperature by the smaller amount dT if we keep the system in equilibrium throughout. The displacement of the equilibrium, therefore, acts as a brake on the imposed change in the intensity factor, in this case the temperature.

The principle of Le Chatelier thus determines the direction in which a monovariant equilibrium is displaced under the influence of a change imposed on one of the variables by which its state is determined. We shall illustrate the application of this principle by a few examples. (For other examples see Khvolson, *Lehrbuch*, iii. p. 474.)

1. *Change in temperature.* (*a*) If, by supplying heat, we raise the temperature of a system consisting of liquid and saturated vapour at constant volume, some of the liquid will evaporate, since evaporation is accompanied by absorption of heat, and therefore tends to diminish the temperature.

(*b*) Raising the temperature of a saturated salt solution causes more salt to dissolve, and therefore increases the solubility, if heat is absorbed in the process of solution. If the heat of solution is positive, *i.e.* if solution of the salt causes heat to be evolved, the solubility will decrease when the temperature is raised.

2. *Change in pressure.* At the melting point solid and liquid are in equilibrium with one another. If the pressure is increased the phase of higher specific volume is converted into the phase of lower specific volume. Usually the solid has the greater density. When this is the case an increase in pressure causes solidification of liquid. If the process is performed adiabatically the heat of fusion set free causes the temperature to rise, and hence the melting point rises with increasing pressure. Increase in pressure produces a lowering in melting point of the few substances, like water, which are denser in the liquid state.

Examples might be multiplied indefinitely to illustrate the manifold phenomena which can be predicted by this principle.

All cases to which the principle of Le Chatelier is applicable can be treated also by thermodynamical methods. The principle of Le Chatelier is, however, usually much easier to apply, and is therefore of use whenever a knowledge of the direction of the displacement is all that is required.

3. The Clausius equation.

Le Chatelier's principle enables us to predict the direction in which the variables of a monovariant system will change under the influence of an imposed change in one of them. By the second law, however, we can obtain more than this merely qualitative result. We can deduce from the second law the amount of the change when the state of the system is given. With this end in view, let us return to the conception of the latent heat of a change of phase in a one-component system as defined on p. 206, viz.

$$-L = U_2 - U_1 + p(v_2 - v_1) = \frac{\partial U}{\partial m} + p(v_2 - v_1). \quad \ldots\ldots(1)$$

When the amount dm of the first phase goes into the second phase at constant temperature, the volume of the whole system changes by $dv = (v_2 - v_1)\,dm$, and its energy increases by the amount

$$\frac{\partial U}{\partial v}\,dv = \frac{\partial U}{\partial m}\,dm = \frac{\partial U}{\partial m}\,\frac{dv}{v_2 - v_1}.$$

Hence, by (1), $$-L = \left(\frac{\partial U}{\partial v} + p\right)(v_2 - v_1). \quad \ldots\ldots(2)$$

By equation (7), on p. 150, we have in general

$$\frac{\partial U}{\partial v}+p=T\frac{\partial p}{\partial T}.$$

Combining this with (2), we have

$$\frac{dp}{dT}=-\frac{L}{T(v_2-v_1)}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

As the system is monovariant, we may write the complete instead of the partial differential coefficient.

This equation was first obtained by Clapeyron, a French engineer who continued the work of Carnot. He derived the equation for the evaporation of a liquid. In its general form it was established by Clausius, and is therefore called the Clausius-Clapeyron, or briefly the Clausius, equation. By means of this equation we can calculate the change in pressure dp produced by an arbitrary change in temperature dT from the quantities L, v_2, v_1, and T, which can all be determined by experiment.

The Clausius equation can be deduced in various ways. According to Helmholtz, the free energy and the total energy of any system are connected by the equation

$$\psi=U+T\frac{\partial \psi}{\partial T}.$$

Let the free energy of a system in equilibrium be ψ_1. If we place the system in a vacuum (*i.e.* under zero pressure) its volume will change as matter is transferred from one phase to another (generally by evaporation) until the equilibrium pressure p has again been established. This spontaneous process is accompanied by a change in the free energy of the system. If ψ_2 is the free energy of the system in its new equilibrium, the change in free energy in the process is equal to $\psi_1-\psi_2$. Let the space available in the vacuum be of such magnitude that exactly unit mass of one phase is changed into another (*e.g.* by the evaporation of unit mass) in the re-establishment of the equilibrium. We have then the two equations

$$\psi_1=U_1+T\frac{\partial \psi_1}{\partial T} \text{ and } \psi_2=U_2+T\frac{\partial \psi_2}{\partial T},$$

and, by subtraction,

$$\psi_1-\psi_2=U_1-U_2+T\frac{\partial(\psi_1-\psi_2)}{\partial T}. \quad \ldots\ldots\ldots\ldots\ldots(4)$$

The decrease in the free energy is equal to the maximum work which can be done by the system when the change of state is carried out reversibly, *e.g.* when the expansion $v_2 - v_1$ proceeds against a pressure p which is equal throughout to the equilibrium pressure.

Hence $$\psi_2 - \psi_1 = p(v_2 - v_1).$$

The change in the total energy is

$$U_1 - U_2 = L + p(v_2 - v_1),$$

by equation (1) (see p. 209). Hence equation (4) becomes

$$p(v_2 - v_1) = L + p(v_2 - v_1) + T\frac{dp}{dT}(v_2 - v_1),$$

or $$\frac{dp}{dT} = \frac{-L}{T(v_2 - v_1)}.$$

Finally, we can deduce equation (3), without using thermodynamic functions (such as U or ψ), by considering a reversible cycle. On p. 138 we found that the efficiency of such a cycle was equal to the temperature drop dT divided by the temperature T of the source of heat. Consider the following cycle (for simplicity the evaporation of a liquid is taken as an example of the method):

1. Evaporation of unit mass (1 mol.) of the liquid at temperature T and vapour pressure p. Here the work done is

$$w_1 = p(v_2 - v_1),$$

and the heat $-L$ is supplied.

2. Adiabatic expansion of the volume v_2 of the saturated vapour to the volume $v_2 + dv_2$ and the pressure $p - dp$, corresponding to the vapour pressure of the liquid at temperature $T - dT$. In this process the temperature falls by an amount dT' which we could calculate by the equation for the adiabatic expansion of a gas (p. 91) if the vapour obeyed the gas laws. In this process the work

$$w_2 = \int_{v_2}^{v_2 + dv_2} p\, dv = p\, dv_2$$

is done by the system.

3. The vapour is heated (or cooled) to $T - dT$ at the constant pressure $p - dp$. Here the quantity of heat $c_2(dT - dT')$ is sup-

plied or given out according as $dT' \gtrless dT$. The work done by the system is $w_3 = (p - dp)\, dv_2'$, where dv_2' is the change in the volume of the gas produced by the change in temperature.

4. Isothermal condensation of the vapour at the pressure $p - dp$ and the temperature $T - dT$. Here the work

$$w_4 = (p - dp)(v_2 + dv_2 + dv_2' - v_1)$$

is done on the system, and the heat $-(L + dL)$ is evolved.

5. The temperature of the liquid is raised by dT, and the heat $c_1 dT$ is absorbed.

In the whole cycle the work $w_1 + w_2 - w_3 - w_4$ has been obtained, *i.e.*

$$\begin{aligned} & w_1 + w_2 - w_3 - w_4 \\ &= p(v_2 - v_1) + p\, dv_2 + (p - dp)\, dv_2 - (p - dp)(v_2 + dv_2 + dv_2' - v_1) \\ &= dp(v_2 - v_1), \end{aligned}$$

neglecting the term $dp \,.\, dv_2$, which is of the second order of magnitude. Hence

$$\frac{w_1 + w_2 - w_3 - w_4}{-L} = \frac{dp(v_2 - v_1)}{-L} = \frac{dT}{T},$$

or

$$\frac{dp}{dT} = \frac{-L}{T(v_2 - v_1)}.$$

All three derivations of the Clausius equation (3) are identical in principle, as they all make use of the second law of thermodynamics. In giving them all in detail we merely wished to show in what diverse ways the second law can be made to lead to concrete experimental results. The most diverse methods have been employed by various investigators in deriving such results. The choice of method depends partly on the nature of the problem and partly also on the task of the investigator. Van't Hoff, for example, generally used reversible cycles in his classical researches. Other physical chemists prefer Helmholtz's equation or the thermodynamic potential, while partial differential equations, as used in the first of the above derivations, are generally found in physical papers.

In the following we shall apply the Clausius equation in some specially important cases and compare the theoretical results with experimental data.

Evaporation of a liquid. The equation

$$\frac{dp}{dT} = \frac{-L}{T(v_2 - v_1)}$$

gives the gradient of the vapour pressure curve. The differential coefficient on the left-hand side of the equation is always found to be positive, *i.e.* the vapour pressure always increases with the temperature. The sign of the right-hand side must therefore also be positive in all cases. Since the specific volume v_2 of the saturated vapour is always greater than that of the liquid, it follows from this that the latent heat L must always be negative. In other words, heat is always absorbed in the conversion of liquid into vapour. On p. 206 we defined the latent heat by the equation

$$-L = U_2 - U_1 + p(v_2 - v_1).$$

As $p(v_2 - v_1)$ can generally be neglected in comparison with $U_2 - U_1$, it follows from the increase of the vapour pressure with temperature that U_2 must always be greater than U_1.

This result could not have been obtained from thermodynamics alone. The kinetic theory of gases and liquids, on the other hand, leads us to conclude that $U_2 > U_1$, as work must be done against the molecular forces when the volume is increased from v_2 to v_1 (see the paragraph on the Joule-Thomson effect, p. 97, and see also p. 152).

The calculation of the vapour pressure curve, *i.e.* of the value of p for any given value of T, can only be carried out by an integration. Thus we have

$$p = -\int \frac{L}{T(v_2 - v_1)}\, dT + \text{const.}$$

The integration is, however, only possible when L and $v_2 - v_1$ are known functions of the temperature. In general this is not the case, but we can obtain an approximate solution of the problem for temperatures which are much below the critical temperature. In this case the specific volume of the liquid is small in comparison with that of the gas, and we may assume that the vapour obeys the gas laws. We may then write

$$v_2 - v_1 = v_2 \text{ and } v_2 = \frac{RT}{p}.$$

Hence $$\frac{dp}{dT} = \frac{-Lp}{RT^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

or $$\frac{d\ln p}{dT} = \frac{-L}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (5a)$$

By integration we obtain the vapour pressure of the liquid at low temperatures in the form :

$$\ln p = \frac{-1}{R}\int \frac{L}{T^2}\,dT + i.$$

i is an arbitrary constant, independent of the temperature, and has a definite value for each liquid. To carry out the integration it is necessary to know L as a function of the temperature. If we restrict ourselves, however, to a small range of temperature $T_2 - T_1$, in which we may regard the vapour pressure as constant, we obtain an approximate solution in the form :

$$\ln \frac{p_2}{p_1} = -\frac{L}{R}\int_{T_1}^{T_2} \frac{dT}{T^2} = \frac{+L}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{-L(T_2 - T_1)}{RT_2T_1}. \quad \ldots (6)$$

The vapour pressure p_2 at temperature T_2 can thus be calculated from the vapour pressure p_1 at T_1 if we know the heat of evaporation.

We must not forget, however, that this calculation is only permissible when we are justified in making the above-mentioned approximations.

In the following table a few examples are given which show how far the equations (5) and (6) are confirmed by experiment. In the numerical calculation L must be taken as the molecular heat of evaporation, since $v_2 = \frac{RT}{p}$ is the volume of 1 mol. L must also be expressed in the same system of units as the gas constant R. In calories and degrees absolute $R = 1{\cdot}985$.

A. For Small Temperature Differences.*

Water : L (by experiment) $= 18 \times 536 = 9650$ cal. $t_0 = 100°$.

$dT°$.	dp mm.	$\frac{dp}{dT}$.	$L_{calc.}$
4·07	103·5	25·43	9660

* Beckmann, Fuchs and Gerhardt, *Zeitschr. f. physikal. Chemie*, **18**, 473 (1895).

Ether : L (by experiment) $= 74 \times 90{\cdot}0 = 6660$. $t_0 = 35°$.

1·020	25·80	25·29	65·60
1·179	29·50	25·01	65·20

Benzene : L (by experiment) $= 78 \times 93 = 7250$.

0·970	22·10	22·78	7350
1·050	23·90	22·76	
1·280	29·05	22·76	

B. For Large Temperature Differences ; Integrated Equation (6).

Water : $L = 9650$ cal.

$t°$.	$p_{\text{determined}}$	$p_{\text{calc.}}$	diff. %.
50	92	101	9·8
60	148·8	159	6·6
70	233·1	243	4·3
80	354·6	363	2·7
90	525·5	531	1·0
100	760	—	—

Ether : $L = 90{\cdot}0 \times 74 = 6660$.

−10	114·7	116	+1·1
0	184·4	186	+0·9
+10	286·8	288	+0·4
+20	432·8	433	0
+35	760	—	—

Benzene : $L = 93 \times 78 = 7250$ cal.

30	120·2	136	14
40	183·6	200	7
50	271·4	286	5
60	390·1	404	3·5
70	547·4	556	1·6
80	752	—	—

As the Clausius equation is strictly accurate (in so far as the laws of thermodynamics are accurate), the deviations from experiment, particularly noticeable in the case of water and benzene, must be due to our having neglected quantities which were not negligible, unless, of course, the experimental results are inaccurate. As v_2 is always very large compared with v_1 at the boiling point, near which all the above data were determined, the deviations must be due to one or both of two causes. Either the vapour does not obey the gas laws, or the latent heat varies

perceptibly even in the small range of temperature for which the calculations were made. If we are considering large ranges of temperature at low temperatures, and hence at low vapour pressures, the latter source of error is the only one we need take into account. Our problem is then to determine the latent heat as a function of the temperature.

We may write L in general as a power series,

$$L = L_0 + \alpha T + \beta T^2 + \gamma T^3 \ldots .$$

The significance of the coefficients becomes apparent on differentiating

$$\frac{dL}{dT} = \alpha + 2\beta T + 3\gamma T^2.$$

On page 107 we found that for vapours which obey the gas laws (equation (10))

$$-\frac{dL}{dT} = c_p - c_1 = -(\alpha + 2\beta T + 3\gamma T^2 \ldots)^*.$$

The constant coefficients of the series can therefore be calculated when the specific heats of vapour and liquid are known at all temperatures. The integration of the Clausius equation thus depends on this purely experimental problem.

The following numerical example shows the variation of the latent heat of water at 100° with the temperature.

Here $c_p = 8{\cdot}0$, $c_1 = 18 \times 1{\cdot}05 = 18{\cdot}9$ cal., and hence

$$-\frac{dL}{dT} = 8{\cdot}0 - 18{\cdot}9 = -10{\cdot}9.$$

Taking $\frac{dL}{dT}$ as constant ($\beta = \gamma = \ldots = 0$) as a first approximation between 50° and 100°, we have

$$+L = +10{\cdot}9T + \text{const.}$$

For 100°, we have

$$+L_{100} = 10{\cdot}9 \times 373 + \text{const.} = -9650 \text{ cal.},$$

and therefore $L_T = -9650 - 10{\cdot}9\,(373 - T)$,

and $L_{50} = -10200$ cal.

* Here L_1, c_p and c_1 refer to 1 mol. of substance. It is also assumed that $L < 0$.

The heat of evaporation of water thus varies by nearly 6 per cent. between 50° and 100°. Allowing for this in the calculation of the vapour pressure, we obtain

$$\frac{d\,ln\,p}{dT}=\frac{9650+10{\cdot}9(373-T)}{1{\cdot}985\,.\,T^2}=\frac{6915}{T^2}-\frac{5{\cdot}5}{T},$$

$$ln\frac{p_2}{p_1}=6910\,\frac{T_2-T_1}{T_1T_2}-5{\cdot}5\,ln\,\frac{T_2}{T_1},$$

$$\log p_2=\log p_1+\frac{6910}{2{\cdot}3}\,\frac{T_2-T_1}{T_1T_2}-5{\cdot}5\log\frac{T_2}{T_1},$$

and for $p_1=760$ mm., $T_1=373°$,

$$\log p_2=2{\cdot}881+8{\cdot}054-3000\,\frac{1}{T_2}+5{\cdot}5\log\frac{T_1}{T_2}.$$

The following table gives the values of the vapour pressure of water between 50° and 100° calculated from this equation.

t° C.	p_{det}	p_{calc}	diff. %.
50	92	95	+3·3
60	148·8	152	+2·2
70	233·1	238	+2·1
80	354·6	359	+1·2
90	525·5	530	+0·86

The differences between the calculated and the determined values are now much smaller than in the first approximation, but are still distinctly perceptible. They would disappear altogether if we allowed for the variation of the specific heats with the temperature.

We should then have

$$ln\,p=-\frac{1}{R}\int\frac{(L_0+\alpha T+\beta T^2+\gamma T^3+\ldots)\,dT}{T^2}+i$$

$$=\frac{L_0}{RT}-\frac{\alpha}{R}\,ln\,T-\frac{\beta}{R}\,T-\frac{\gamma}{2R}\,T^2\ldots+i.$$

This equation gives the vapour pressure of any liquid for all temperatures at which the vapour obeys the gas laws. The constants L_0, α, β, γ, ..., and i vary for each substance. The equation also applies to solid bodies if L_0 is taken to be the heat of sublimation. The values of the constants and their relationship to one another for various substances cannot be calculated by thermodynamics.

The most diverse empirical formulae for the variation of vapour pressure with temperature have been proposed by various investigators (see Winkelmann, *Handb. d. Physik*, vol. iii. p. 949).

Regnault used the following equation in his numerous investigations:

$$\log p = a + b\beta^{t-t_0} + c\gamma^{t-t_0}.$$

a, b, c, β, γ are constants characteristic of the substance, and t_0 is the lowest temperature at which the vapour pressure was observed. The term $c\gamma^{t-t_0}$ is generally found to be very small. β has nearly the same value for all substances.

A formula, deduced by Kirchhoff from theoretical considerations, has also been employed with success, viz.

$$\log p = A - \frac{B}{T} - C \log T.$$

It is also known as Rankine's or as Dupré's formula. We see at once that this formula is a particular case of the general formula given above, if we put

$$A = i, \quad -B = \frac{L_0}{R}, \quad C = \frac{+\alpha}{R} \text{ and } \beta, \gamma, \ldots = 0.$$

Recently Nernst has proposed a formula * (based partly on the theorem of corresponding states), which is also a particular case of the general formula, viz.

$$ln\, p = \frac{L_0}{RT} + \frac{3{\cdot}5}{R} ln\, T - \frac{\beta T}{R} + i.$$

According to this formula, the constant α has the same value $-3{\cdot}5$ for all substances, *i.e.* the molecular heat c_p of the vapour at the absolute zero is greater by 3·5 than the molecular heat of the liquid. Modern investigations on specific heats at low temperatures have shown that this is not the case, so that Nernst's formula also is only of value as an empirical interpolation formula.

At higher temperatures, in the neighbourhood of the critical point, all these approximations become meaningless, as the volume of the liquid can no longer be neglected in comparison

* This formula is discussed fully in *Thermodynamics and Chemistry*, New York, 1907.

with the volume of the vapour. We can therefore say very little about the form of the vapour pressure curve near the critical point, as the experimental determination of L and of v_2 and v_1 is very troublesome. At the critical point L and $v_2 - v_1$ become zero simultaneously, and the differential coefficient $\frac{dp}{dT}$ becomes indeterminate. The vapour pressure curve ceases at the critical point.

The relationships which we have just been considering apply only to cases in which the boundary between the liquid and the saturated vapour is a plane surface. The vapour pressure at a curved surface is not the same as at a plane surface. The reason for this will be discussed in a subsequent paragraph (capillarity).

The dependence of the vapour pressure on the external pressure. The vapour pressure of a liquid, like all other physical properties, varies with the external pressure on the liquid. If the liquid is subjected to the pressure of an inert gas, the partial pressure of the vapour is not equal to the vapour pressure of the liquid at the same temperature. We can calculate the relationship between the vapour pressure p and the external pressure P at constant temperature, as follows : *

Consider a liquid of specific volume V enclosed in a cylinder furnished with a movable piston A and a partition B which is permeable to the vapour but not to the liquid. On the other side of B let there be another movable piston C (Fig. 23). Let the pressure on A be the external pressure P, and the pressure on C be the vapour pressure p of the liquid when subjected to the pressure P. Let us now perform the following cycle at constant temperature :

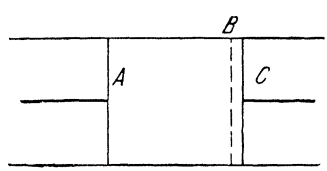


FIG. 23.

1. A quantity dm of the liquid is evaporated while the pressure P is kept constant. Both pistons will move to the right, C corresponding to volume $v\,dm$ where v is the specific volume of

* Cf. B. Schiller, *Wied. Ann.* **53**, 396 (1894); and Callendar, *Zeitschr. f. physikal. Chemie*, **63**, 645 (1908).

the vapour at the pressure p, and A corresponding to the much smaller volume of the liquid $V\,dm$. The work done by the system is

$$w_1 = p\,.\,v\,.\,dm - P\,.\,V\,.\,dm.$$

2. Both pressures P and p are increased simultaneously by dP and dp in such a manner that $p+dp$ is the vapour pressure of the liquid under the pressure $P+dP$. In this process neither evaporation nor condensation takes place, and the work done on the system is $w_2 = (V - V\,dm)\,dP + v\,dm\,dp$.

3. A quantity of vapour dm is condensed while the pressures are kept constant at $P+dP$ and $p+dp$. Neglecting, as of the second order of magnitude, the changes in specific volume of liquid and vapour produced by the increases in pressure dP and dp respectively, we obtain for the work done on the system

$$w_3 = (P+dp)\,V\,dm - (p+dp)\,v\,dm.$$

4. The pressure is reduced from $P+dp$ to P. The work done by the system is

$$w_4 = +V\,dp.$$

As the whole cycle is carried out at constant temperature, the total work done must be zero, *i.e.*

$$w_1 - w_2 + w_3 + w_4 = 0.$$

If this were not so and work had been done on or by the system by interchange of heat with the surroundings, we could use the cycle to obtain perpetual motion of the second kind.

Dividing by dm, we have therefore

$$pv - pV - \frac{V\,dP}{dm} + V\,dP - v\,dp + PV + V\,dp - pv - v\,dp + \frac{V\,dP}{dm} = 0,$$

or

$$2V\,dP - 2v\,dp = 0,$$

and hence

$$\frac{dp}{dP} = \frac{V}{v}.$$

As the specific volume v of the vapour is much greater at low temperatures than that of the liquid, the change in vapour pressure produced by an increase in the total pressure is small.

For the purpose of a rough calculation of this change in vapour pressure we may divide by p and obtain, since $pv = RT$,

$$ln \frac{p_1}{p_2} = \frac{1}{RT} \int_{P_2}^{P_1} V \, dp.$$

For nearly equal values of P_1 and P_2 we may replace v by its mean value between P_1 and P_2, and obtain

$$\log \frac{p_1}{p_2} = \frac{V(P_1 - P_2)}{2{\cdot}3RT}.$$

Using this formula we can calculate, for example, the vapour pressure p_1 of water at 0° and a pressure of 1 atmosphere. Here the vapour pressure $p_2 = 4{\cdot}579$ mm. (liquid under pressure p_2), and we have

$$\log \frac{p_1}{p_2} = \frac{0{\cdot}018}{2{\cdot}3 \times 22{\cdot}4} = 0{\cdot}00035,*$$

and hence $p_1 = 1{\cdot}001$, $p_2 = 4{\cdot}583$.

The difference is thus less than 1 per thousand, and is probably within the experimental error. In vapour pressure measurements it should be noted that the static method gives the true vapour pressure, while the dynamic method gives the vapour pressure at atmospheric pressure. In most cases, however, both methods will lead to practically the same results. For very small values of T, as in determinations of the vapour pressure of liquefied "permanent" gases, we might expect to find appreciably different results by the two methods. A rough calculation shows that for liquid nitrogen at −208° C. the dynamic method should give a 4 per cent. higher result than the static method.

Application to the process of fusion. Variation of the melting point with pressure. As a second example of the application of the Clausius equation, let us consider the change of a pure substance from the solid to the liquid state. By the phase rule we have two phases and one component, and hence one degree of freedom. Each pressure will therefore correspond to a definite melting point, at which solid and liquid are in equilibrium. The melting point is therefore a function of the pressure on the system according to the equation

$$\frac{dp}{dT} = \frac{-L}{T(v_2 - v_1)}.$$

* The molecular volume of water is 18 c.c. = ·018 litre.

It is usual to determine the melting point at varying pressure, taking the pressure as independent variable. We shall therefore write the equation in the form

$$\frac{dT}{dp} = \frac{T(v_2 - v_1)}{-L}.$$

Here L is the heat of fusion, which is set free in the transition from the phase 1 to the phase 2, v_1 and v_2 are the specific volumes of the two phases. The melting point will rise or fall with the pressure according as L and $v_2 - v_1$ have the same or opposite signs. L is always negative, and for most substances $v_2 > v_1$, *i.e.* fusion is generally accompanied by an increase in volume. Thus the melting point generally rises as the pressure is increased. For water which contracts on freezing the reverse is true. Consequently ice can be liquefied by increasing the pressure at constant temperature, while most other bodies solidify under the same circumstances.

A quantitative proof of the above equation was given for water by James and William Thomson in 1849. This was one of the first quantitative applications of the second law to physical-chemical equilibria. James Thomson calculated the depression of the freezing point of water from the known values of L and $v_2 - v_1$ to be 0·0075° C. per atmosphere.

His brother William found by experiment

for 8·1 atm. 0·059° instead of 0·061,
„ 16·8 „ 0·129° „ 0·126.

As most other substances have a smaller heat of fusion than water, the change in their melting point as the pressure is increased will be greater than for water. Thus, for acetic acid de Visser found 0·0244° and calculated 0·0242° per atmosphere.

The experimental determination of the melting point at high pressures is generally somewhat difficult. In some cases it is easier to determine the pressure at which the fusion or solidification of a substance in a closed vessel comes to a stop at constant temperature. A very simple and ingenious "manocryometer" was invented by de Visser for this purpose (Fig. 24). The substance in A is separated by a column of mercury

from the air column B. The apparatus filled with the solid substance is placed in a thermostat above the temperature at which fusion begins at atmospheric pressure. As fusion proceeds, the volume, and hence the pressure, increase until equilibrium is reached at the melting point corresponding to the temperature of the bath. The pressure is calculated from the compression of the air column B, which serves as manometer. A number of

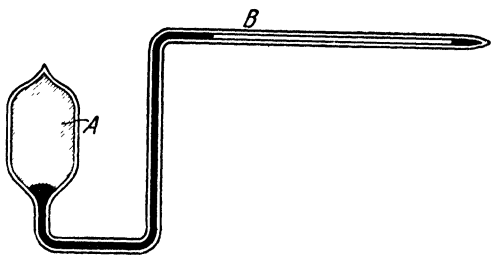


FIG. 24.

other methods which can also be employed at higher pressures have been elaborated and used by Tammann and his colleagues.*

The above equation has recently been confirmed with a high degree of accuracy by Johnston and Adams.† They determined the melting points of a number of metals at pressures up to 2000 atmospheres, and obtained the following table:

Metal.	T.	L (per gr.).	$v_1 - v_2$.	Δt per 1000 atm.	
				calc.	found.
Sn	273+231	14·25	0·003894	+3·34	+3·28
Cd	273+320	13·7	0·00564	+5·91	+6·29
Pb	273+271	5·37	0·003076	+8·32	+8·03
Bi	273+327	12·6	0·00342	−3·56	−3·55

Tammann carried out elaborate investigations to decide whether the melting point increases continuously as the pressure is increased, whether it goes through a maximum or whether the pressure temperature curve comes to a stop at

* *Krystallisieren und Schmelzen.*

† *Zeitschr. f. anorgan. Chemie*, **72**, 11 (1911).

a definite point like the vapour pressure curve of a liquid at the critical point. The latter alternative would mean that the solid and liquid states were identical above a certain temperature and pressure, and that the transition from the one state to the other could be carried out continuously, as in the case of liquids and gases. Ostwald and Poynting assumed the existence of a critical point of this kind between the liquid and the solid state, while Tammann's researches lead to the opposite conclusion.*

We can formulate the problem in terms of our equation as follows: The temperature coefficient will have the same sign as long as L and $v_2 - v_1$ are of the same sign. It will become zero, *i.e.* the melting point (as a function of the pressure) will be a maximum or a minimum when the specific volumes of the solid and the liquid are equal to one another. It will be indeterminate, *i.e.* the curve will end at a critical point, if the latent heat and the difference in volume become zero at the same temperature. The integration of our equation is only possible when the latent heat and the difference in volume are known as functions of the temperature or pressure, which is not usually the case. (The variation of the latent heat with the temperature is determined by the difference between the two specific heats and its variation with the temperature: see p. 103.)

If a critical point solid-liquid exists, both phases would have the same equation of condition, analogous to Van der Waals' equation for liquids and gases. From considerations based on the molecular theory, Tammann concludes that this is not the case. A liquid can change continuously into an amorphous glass-like solid, but never into an anisotropic crystal. It is difficult to conceive of continuous transition from a state of disordered motion, such as we must assume in the liquid and gaseous states, to the ordered arrangement of the atoms and molecules in a crystal.

These considerations are confirmed by experiment. So far a critical point between solid and liquid has never been observed. A number of investigations appear to show that such a critical

* Cf. *Ann. d. Physik*, **36**, 1027 (1911).

point does not exist. Damien, Tammann, and others have found that the melting point increases with pressure according to the equation

$$T = a + bp - cp^2,$$

where the term in p^2 has a negative coefficient. From this equation we conclude that the melting point T would pass through a maximum at high pressures. The position of the maximum can be calculated from the constants b and c. We have

$$\frac{dT}{dp} = b - 2cp, \text{ and hence } p_{max} = \frac{b}{2c}.$$

At this pressure the substance would melt without change in volume. For most substances the change in volume on melting is positive, so that the compressibility of the liquid phase must be greater than that of the solid phase.

The pressures at which the melting point reaches the maximum are generally very high. From the constants of the above equation, Tammann has calculated the following values :

Substance.	$t°$ at 1 atm.	$t°$ max.	at p atm.
Phosphorus	43·9	438	14400
Benzophenone	47·7	189	10200
Naphthalene	79·8	201	11500
Benzene	5·3	113	7620
Hydrocyanic acid	−13·4	+81	7400
Acetic acid	16·6	67·2	4600
Dimethyl-ethyl carbinol	−9·0	+36·5	4750

Tammann succeeded only in a single case in determining the melting point at and above the maximum. Glauber's salt Na_2SO_4, $10H_2O$ melts at 32·6° under 1 atm. pressure. The melting point rises at first as the pressure is increased, but at 3000 atm. it is only 30·0°. The maximum increase in the melting point of 0·122° is reached at a pressure of 460 kg. per square centimetre.

For a number of substances Tammann determined the change in volume on melting and the increase in the melting point with

pressure, and calculated the latent heat of fusion from these data. The results are given in the following table :

Substance.	p in atm.	$t°$.	$v_2 - v_1$ c.c. per 1 gr.	l.
Dimethyl-ethyl carbinol -	215	−5·45	0·0403	11·9
	2515	+30·00	0·0144	11·0
Benzene - - - -	1	5·43	0·1301	30·6
	2620	66·00	0·0738	32·6
	3250	77·96	0·0693	—
Naphthalene - - -	1	80·10	0·1458	34·1
	1776	138·80	0·1054	32·5
Phosphorus - - -	1	43·94	0·0191	5·03
	2155	100·18	0·0148	5·19
Benzophenone - - -	1	48·00	0·0853	23·4
	1910	95·00	0·0679	25·8

These figures would indicate that $v_2 - v_1$ approaches zero, while the latent heat remains finite, as the pressure is increased.

The transition point between two allotropic modifications of the same substance is, like the melting point, a function of the temperature. In the equation

$$\frac{dT}{dp} = \frac{-T(v_2 - v_1)}{L},$$

which, of course, applies to this case also, L is the latent heat of transition, and v_2 and v_1 are the specific volumes of the two solid modifications.

CHAPTER VIII.

THEORY OF SOLUTIONS.

1. Thermodynamic relationships.

We shall now consider two component systems, with the restriction, in the first instance, that the two components can form no chemical compounds with one another capable of appearing as separate phases. In other words, the two components are to form only physical mixtures or solutions with one another (see Nernst, *Lehrbuch*, 6th edn. p. 99). A general definition of the term solution has already been given (p. 193). The gaseous portion of a many component system is strictly speaking a solution, as it consists of only one phase which contains all the components. Some of them may be present in very minute quantities, but we must ascribe a finite vapour pressure to every substance at all temperatures on account of the continuity of physical quantities. In many cases, of course, the vapour pressure is too small to be measured (most solids, for example), so that we may neglect the partial pressure of these substances in the vapour. We shall show that if the dissolved substances have no appreciable vapour pressure, the vapour pressure of the solution is always less than that of the pure solvent.

In the history of physical chemistry dilute solutions were regarded as specially important, as their behaviour is governed by simple laws. A dilute solution is a solution in which the concentration of one component (the solvent) preponderates greatly over that of all the others. The physical properties of dilute solutions differ therefore only slightly from those of the pure solvent. Their thermal properties are connected with the

depression of the vapour pressure by thermodynamical relationships which will be deduced in the following.

Vapour pressure of solutions. The Clausius equation can be applied directly to the evaporation of a solution if we make the restriction that the concentration of the solution shall not alter appreciably when 1 mol. of the solvent is evaporated, which is the case if we are dealing with a very large volume of the solution. The system solution-vapour is then monovariant, and has a definite vapour pressure p at every temperature. If the dissolved substance (solute) has no appreciable vapour pressure, this pressure p is equal to the partial pressure of the solvent. If not, the vapour pressure is equal to the total pressure, *i.e.* to the sum of the partial pressures of all the components of the solution. In the meantime we shall restrict ourselves to the first case.

The variation of the vapour pressure with the temperature is then given by

$$\frac{dp}{dT} = \frac{-L}{T(v_2 - v_1)},$$

or, neglecting the volume of the liquid and applying the gas laws to the saturated vapour,

$$\frac{d\ln p}{dT} = \frac{-L}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$-L$ is the amount of heat which must be supplied to the solution in order to vaporise 1 mol. of the solvent at constant pressure and temperature.

For the pure solvent, we have the corresponding equation

$$\frac{d\ln p_0}{dT} = \frac{-L_0}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In general, L is not equal to L_0. The difference $L_0 - L = L_v$ is the amount of heat evolved when a large volume of the liquid is diluted by the addition of 1 mol. of solvent. This quantity is called the heat of dilution of the solution. Subtracting (2) from (1), we have

$$\frac{d\ln \frac{p}{p_0}}{dT} = -\frac{L - L_0}{RT^2} = +\frac{L_v}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The quotient $\frac{p}{p_0}$ therefore increases with the temperature if the heat of dilution is positive, and diminishes if it is negative. The relative lowering of the vapour pressure is defined as the quotient $\frac{p_0 - p}{p}$. The relative lowering therefore increases with the temperature for solutions which become cooler on dilution, and diminishes for solutions which have a positive heat of dilution.

This result was first deduced by Kirchhoff, and has hitherto been qualitatively confirmed in every case. Quantitative determinations are difficult to carry out, as the relative lowering of

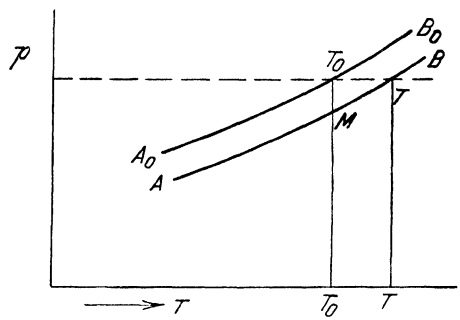


FIG. 25.

the vapour pressure is very small and slight errors have a large influence on the result.*

In very dilute solutions the heat of dilution is found by experiment to be very small, and may be neglected in practice (just as the dilution of perfect gases involves no change in their energy). For such a solution the relative lowering of the vapour pressure is the same at all temperatures. This law has been confirmed by v. Babo in a large number of cases.

The raising of the boiling point. The boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure. At the boiling point of the pure solvent the vapour pressure of the solution is less than one atmosphere, and hence the solution must have a higher boiling point than the pure solvent. This is shown in Fig. 25, in which AB is the vapour pressure curve of

* See Kirchhoff, *Pogg. Ann.* **104** (1856); H. v. Helmholtz, *Wied. Ann.* **27**, 542 (1886); Nernst, *Lehrbuch*, 6th ed. p. 116.

the solution and A_0B_0 that of the pure solvent. For very dilute solutions the increase in the boiling point $T-T_0$ can easily be calculated. From the figure we have

$$\frac{TT_0}{T_0M}=\cot MTT_0,$$

or

$$\frac{T-T_0}{p_0-p}=\frac{1}{\frac{dp_0}{dT}}=\frac{RT_0^2}{-L_0p_0}; \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

and hence

$$T-T_0=\frac{RT_0^2}{-L_0}\cdot\frac{p_0-p}{p_0},$$

if $T-T_0$ and $p-p_0$ be taken so small that the portion MT of the curve may be regarded as a straight line.

A more general equation, applicable to more concentrated solutions, may be obtained as follows. Integrating 1 between the boiling point T_0 of the solvent and the boiling point T of the solution, we have

$$ln\frac{p_T}{p_{T_0}}=\frac{L}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right).$$

If the evaporation proceeds at atmospheric pressure, $p_T=1$, and hence

$$\frac{1}{T_0}-\frac{1}{T}=\frac{R}{L}ln\,p_{T_0}, \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

and the raising of the boiling point is given by

$$T-T_0=\frac{RT_0^2\,ln\,p_{T_0}}{L-RT_0\,ln\,p_{T_0}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(5a)$$

The raising of the boiling point can therefore be calculated from the vapour pressure of the solution at the boiling point of the pure solvent, if the heat of evaporation remains constant in the interval $T-T_0$. Otherwise a mean value of L must be substituted in equation (5a). It is easy to show that (5) approximates to (4) when $L=L_0$, and $\frac{p}{p_0}$ is so nearly equal to unity that we may put

$$ln\frac{p_0}{p}=\frac{p_0-p}{p}.*$$

* By the formula $ln(1+\epsilon)=\epsilon$ for small values of ϵ. $\left(\epsilon=\frac{p_0-p}{p}\right)$.

Freezing point of solutions. The freezing point of a solution is always lower than that of the pure solvent. This may be seen at once from Fig. 26, which differs from Fig. 25 only by the addition of the vapour pressure curve CNP of the solid solvent. The abscissa of P, the intersection of CP and A_0B_0, is the freezing point T_0 of the pure solvent, and the abscissa of the corresponding intersection N is the freezing point of the solution, for at these points the solid solvent is in equilibrium with solvent and solution

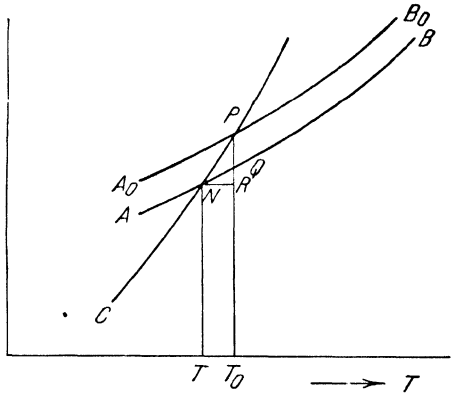


FIG. 26.

respectively. The lowering of the freezing point T_0-T, (NR) may be calculated for dilute solutions as follows:

In triangle PNR,

$$\tan PNR=\frac{RP}{NR}=\frac{PQ+QR}{NR}=\frac{dp}{dT}=\frac{-L_s\cdot p}{RT^2},$$

where L_s is the heat of sublimation of the solid solvent.

Further,

$$PQ=p_0-p \text{ (for } T_0) \text{ and } \frac{QR}{NR}=\tan QNR=\frac{-Lp}{RT^2},$$

where L is the heat of evaporation of the solution.

Hence

$$\frac{p_0-p}{T_0-T}=\frac{-L_s\cdot p}{RT^2}+\frac{L\cdot p}{RT^2}.$$

For $L=L_0$ we have $L_s-L=L_s-L_0=W$, the molecular heat of fusion of the pure solvent, and hence

$$T_0-T=\frac{-RT_0^2}{W}\cdot\frac{p_0-p}{p}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

The formula for the lowering of the freezing point is thus quite analogous to the formula for the raising of the boiling point, and differs from it in that the heat of fusion takes the place of the heat of evaporation.

For concentrated solutions, for which the heat of dilution has a finite value and for which the lines NP and NQ are always curved, we can deduce a more accurate equation as follows:

For the solution we have

$$\frac{d\,ln\,p}{dT}=\frac{-L}{RT^2},$$

which, integrated between the freezing point T_0 of the pure solvent and any arbitrary temperature T, becomes

$$ln\,p=\frac{L}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)+ln\,p_{T_0}.$$

We have also the corresponding equation for the solid solvent

$$ln\,p_0=\frac{L_s}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)+ln\,p_{0_{T_0}}.$$

At the freezing point of the solution (T) the two curves intersect so that

$$\frac{L}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)+ln\,p_{T_0}=\frac{L_s}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)+ln\,p_{0_{T_0}},$$

or

$$\frac{1}{T}-\frac{1}{T_0}=\frac{R}{L-L_s}.ln\left(\frac{p_0}{p}\right)_{T_0}=\frac{-R}{W+L_v}ln\left(\frac{p_0}{p}\right)_{T_0}. \quad \ldots\ldots(7)$$

Equations (5) and (7) are valid when the saturated vapour obeys the gas laws (which we may generally assume to be the case at the freezing point), and when the quantities L are constant in the interval $T-T_0$. Otherwise mean values in the interval between T and T_0 must be taken.

2. Mixture of liquids.

We shall now consider solutions of two substances, both of which have a measurable vapour pressure, such as mixtures of water and alcohol, or of two other volatile, miscible liquids. Let the vapour pressure of the liquid A be P_a, that of B be P_b, and let the vapour pressure of the solution be P. P is then

always a function of the proportions of the two liquids in the mixture as well as of the temperature.

The nature of this function cannot be deduced thermodynamically, but the condition $P<P_a+P_b$ must always be fulfilled.

P is the sum of the partial pressures of the two components in the mixture p_a and p_b, so that $P=p_a+p_b$ and also $p_a<P_a$ and $p_b<P_b$. In the simple case in which the two liquids have no influence on one another in the mixture, many of the physical properties of the mixture (solution) can be calculated by the law of mixtures from those of the pure components (*e.g.* specific gravity, refractive index, dielectric constant). If the law of mixtures also applies to the vapour pressure, we have

$$p_a=\frac{1}{1+x}P_a$$

and

$$p_b=\frac{x}{1+x}P_b,$$

where x is the number of mols of B dissolved in 1 mol of A.

The ratio $\frac{1}{1+x}=\nu_a$ is called the mol fraction of A, and $\frac{x}{1+x}=\nu_b$, the mol fraction of B in the solution.

We have then $\nu_a=1-\nu_b$, and

$$P=p_a+p_b=\frac{P_a+xP_b}{1+x}=\nu_aP_a+(1-\nu_a)P_b,$$

i.e. a linear function of ν_a.

For $x=0$ (pure A), we have $\nu_a=1$ and $p_a=P=P_a$.

,, $x=\infty$ (pure B), we have $\nu_a=0$ and $p_b=P=P_b$.

For all other values of x the quantities p_a, p_b and P vary linearly with the mol fraction, as shown in Fig. 27.

This simple linear variation of the vapour pressure is found very rarely in practice. In general the components influence one another in such a manner that the physical properties of the solution are no longer additive functions of the properties of the pure components. The vapour pressure curve (at constant temperature) may then be either concave or convex to the axis of abscissae, and may even have maxima or minima.

Examples of each kind have been found in nature with different pairs of liquids.*

The variation with temperature of the partial pressures p_a and p_b of a solution of composition x can be calculated from the heat of mixture, with the aid of the Clausius equation.

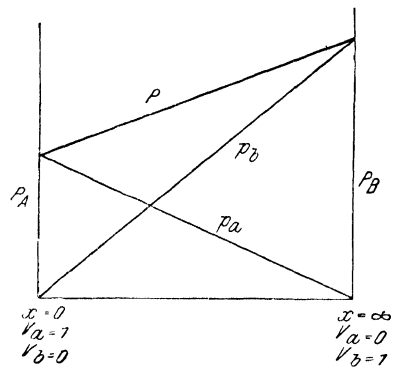


FIG. 27.

For the two components in the solution, we have the two equations

$$\frac{d \ln p_a}{dT} = \frac{-L_a}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (a)$$

and

$$\frac{d \ln p_b}{dT} = \frac{-L_b}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (b)$$

The quantities L_a and L_b are the amounts of heat which must be supplied to the solution in order to evaporate 1 mol of the substances A and B respectively. Thus L_a is the heat of evaporation ($-L^\circ_a$) of the pure substance A, plus the heat $L_{v,a}$ which is set free when the solution x is diluted with 1 mol of A (see p. 228), *i.e.*

$$+L_a = +L_a^\circ - L_{v,a}.$$

Similarly,

$$+L_b = +L_b^\circ - L_{v,b}.$$

The sum $L_m = L_{v,a} + xL_{v,b}$ is the amount of heat which is set free when the solution x is diluted with 1 mol of A and x mols of B. As the concentration of the solution is not altered by this process, L_m must be equal to the heat set free on mixing

* Cf. v. Zawidzki, *Zeitschr. f. physikal. Chemie*, **35**, 129 (1900).

1 mol of A with x mols of B. In other words, L_m is the heat of mixture.

Multiplying (b) by x and adding (a), we obtain

$$\frac{d\,ln\,p_a}{dT}+x\frac{d\,ln\,p_b}{dT}=\frac{-L_a^\circ-xL_b^\circ+L_m}{RT^2}.$$

Combining this with

$$\frac{d\,ln\,P_a}{dT}=\frac{-L_a^\circ}{RT^2},\text{ etc.},$$

we have

$$\frac{d\,ln\frac{p_a}{P_a}}{dT}+x\frac{d\,ln\frac{p_b}{P_b}}{dT}=\frac{+L_m}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

This equation was first deduced by Nernst in a different manner.* Bose confirmed the equation experimentally for the special case of rectilinear vapour pressure curves.† In this case the left-hand side of the equation becomes

$$\frac{d\,ln\frac{1}{1+x}}{dT}+x\frac{d\,ln\frac{x}{1+x}}{dT}.$$

As the logarithms are both independent of T, their differential coefficients must vanish, so that the heat of mixture is zero. Bose found this to be actually the case for mixtures of methyl and ethyl alcohol.

We see, therefore, that only those liquids which can be mixed without evolution of heat will give rectilinear vapour pressure curves when dissolved in one another. This condition, however, is not sufficient to ensure the linear variation of the partial pressures with the mol fraction, for $\frac{p_a}{P_a}$ and $\frac{p_b}{P_b}$ might be any other functions of x, and still be independent of T.

If the heat of mixture is positive, these quotients will increase as the temperature is raised, and the relative lowering of the vapour pressure on mixing will diminish. If the heat of mixture is negative, the reverse is the case.

* *Theoretische Chemie*, 6th ed. p. 115.

† E. Bose, *Zeitschr. f. physikal. Chemie*, **58**, 621 (1907). See also Zawidzki, *l.c.*

As has already been stated, the laws of thermodynamics can give us little information as to the way in which the lowering of the vapour pressure depends on the mol fraction. We can show, however, by pure thermodynamics that the changes in the two partial pressures with increasing x must be in some relationship to one another. It follows from the phase rule alone that this must be so. A solution of two substances in equilibrium with their saturated vapour has only two degrees of freedom. If the temperature and the mol fraction are given, the system is uniquely determined. As the equation $P = p_a + p_b$ can be satisfied by an infinite number of values of p_a and p_b, there must be some other relationship between p_a and p_b. This relationship was first discovered by Duhem, and has since been fully investigated and deduced in other ways by Margules and others.*

To derive this equation it is necessary to employ a different method from that used hitherto in this chapter. The Clausius equation can only be applied to variations of pressure with temperature, and is useless where isothermal processes are concerned. We shall, therefore, make use of another consequence of the second law, namely, that no work can be done when two systems in equilibrium with one another are mixed. Thus no work can be done when 1 mol of the component A and x mols of the component B are transferred isothermally from one portion of a solution of composition x to another portion of the same solution.

Consider two very large, equal portions of a solution of composition x. Let each of these portions be furnished with a membrane permeable only to the component A, and also with a membrane permeable only to B.

Consider now the following series of reversible and isothermal processes :

1. Let 1 mol of A be allowed to diffuse out of the first solution through the semipermeable membrane. In this process the partial pressure of A in solution 1 diminishes from p_a to $p_a - dp_a$, while that of B increases from p_b to $p_b + dp_b$. The vapour might be made to do work (in pushing back a piston, for example)

* For the literature, see Zawidzki, *loc. cit.*

as it diffuses out through the semipermeable membrane. The maximum work obtainable is

$$w_1 = \int_0^{v_a + dv_a} p\, dv.$$

Since p varies only by a differential, we may substitute its mean value, viz. $p_a - \frac{1}{2}dp_a$ in this integral and obtain

$$w_1 = (p_a - \tfrac{1}{2}dp_a)\int_0^{v_a+dv_a} dv = p_a v_a - \tfrac{1}{2}v_a dp_a + p_a dv_a.$$

2. Compress the mol of A until its pressure has again become equal to p_a and its volume to v_a.

Here

$$w_2 = -p_a dv_a.$$

3. Transfer the mol of A into solution 2, through the semipermeable membrane (by forcing it through with a piston, for example). In this process the concentration of A in solution 2 increases, and its partial pressure rises from p_a to $p_a + dp_a$, while that of B falls from p_b to $p_b - dp_b$.

The maximum work obtainable here is

$$w_3 = -p_a v_a - \tfrac{1}{2}v_a dp_a.$$

Thus the work done in the transference of A is

$$w_A = w_1 + w_2 + w_3 = -v_a dp_a.$$

Now let x mols of B be transferred from solution 1 to solution 2 in an exactly similar manner. The maximum work obtainable can be calculated in the same way as before, and is found to be

$$w_B = -xv_b dp_b.$$

At the conclusion of this operation both solutions have returned to their original concentration, and the result of the whole series of operations has merely been to transfer 1 mol of A and x mols of B from 1 to 2.

The work done in the whole process must, therefore, be zero,

$$i.e.\quad -v_a dp_a - xv_b dp_b = -\frac{RT}{p_a}dp_a - x\frac{RT}{p_b}dp_b = 0.$$

or

$$\frac{dp_a}{dp_b} = -x\frac{p_a}{p_b}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9a)$$

or $$\frac{d\,ln\,p_a}{d\,ln\,p_b} = -x, \quad \ldots\ldots(9b)$$

or $$\frac{d\,ln\,p_a}{dx} + x\frac{d\,ln\,p_b}{dx} = 0. \quad \ldots\ldots(9c)$$

Substituting for x the mol fraction

$$\nu_a = \frac{1}{1+x}\left(x = \frac{1-\nu_a}{\nu_a}\right),$$

equations (9a), (9b) and (9c) become

$$\frac{dp_a}{dp_b} = \frac{1-\nu_a}{\nu_a} \cdot \frac{p_a}{p_b}, \quad \ldots\ldots(9d)$$

$$\frac{d\,ln\,p_a}{d\,ln\,p_b} = \frac{1-\nu_a}{\nu_a} \quad \ldots\ldots(9e)$$

and $$\frac{d\,ln\,p_a}{d\nu_a} + \frac{1-\nu_a}{\nu_a} \cdot \frac{d\,ln\,p_b}{d\nu_a} = 0. \quad \ldots\ldots(9f)$$

We can draw certain conclusions from the equations 9 as to the direction of the p_a and p_b curves (p_a and p_b as ordinates, and mol fraction ν_a as abscissae (see Figs. 27-29)).

1. The p_a curve is a straight line, viz. $p_a = \nu_a P_a$. Then the p_b curve must also be a straight line, viz. $p_b = (1-\nu_a)P_b$. For it follows from (9f) that if $\frac{d\,ln\,p_a}{d\nu_a} = \frac{1}{\nu_a}$, then

$$\frac{d\,ln\,p_b}{d\nu_a} = -\frac{1}{1-\nu_a}$$

and $ln\,p_b = ln\,(1-\nu_a)$, $p_b = (1-\nu_a)P_b$.

2. If the p_a curve is convex to the ν_a axis, the p_b curve must also be convex (Fig. 28). According to Margules the two partial pressure curves may be represented approximately by the equations

$$p_a = P_a \cdot \nu_a^{\,n}, \quad p_b = P_b(1-\nu_a)^n,$$

where n is an empirical positive constant. If the p_a curve is convex, we have

$$\frac{dp_a}{d\nu_a} = n \cdot P_a \cdot \nu_a^{\,n-1} > 0,$$

and therefore, since $n > 1$,

$$\frac{d^2p_a}{d\nu_a^{\,2}} = n(n-1)P_a\nu_a^{\,n-2} > 0,$$

and also $$\frac{dp_b}{dv_a} = -nP_b(1-v_a)^{n-1} < 0,$$

and $$\frac{d^2p_b}{dv_a^2} = +n(n-1)P_b(1-v_a)^{n-2} > 0.$$

The second differential coefficients of p_a and p_b are thus both positive, and hence both curves are convex to the v_a axis.

3. For the same reason it follows that the p_b curve is always concave when the p_a curve is concave to the v_a axis (Fig. 29).

Theory of fractional distillation. We shall now discuss some consequences of Duhem's equation which are of importance in

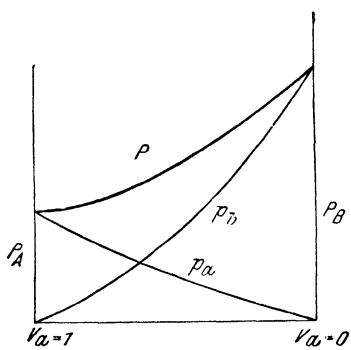


FIG. 28.

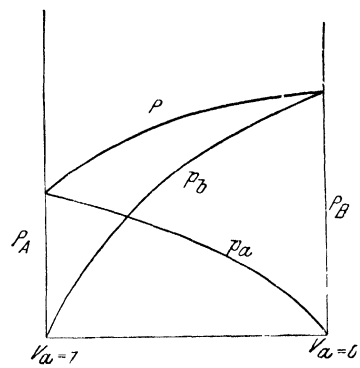


FIG. 29.

the fractional distillation of mixtures of liquids. As we have already shown, the total vapour pressure P of the mixture passes through a continuous series of values between P_a and P_b as x increases from 0 to ∞. The P, v curve may be rectilinear or curvilinear, and may have a maximum or a minimum. If P increases with x, *i.e.* if $\frac{dP}{dx} > 0$, then $\frac{dp_a}{dx} + \frac{dp_b}{dx} > 0$ and $\frac{dp_a}{dp_b} > -1$. Hence, by (9*a*),

$$-x\frac{p_a}{p_b} > -1, \quad \frac{xp_a}{p_b} < 1 \text{ or } \frac{p_b}{p_a} > x.$$

x is the ratio of the concentrations of the two components in the liquid phase, and $\frac{p_b}{p_a}$ is the same ratio for the gaseous phase. Thus in the vapour there is a greater concentration of

the component which produces an increase in the total vapour pressure when added to the mixture. When the mixture is distilled, $\frac{p_b}{p_a} > x$ mols of B will be removed from the liquid for each mol of A. The liquid therefore becomes less and less rich in B as the distillation proceeds. At constant temperature the vapour pressure of the liquid diminishes, and if the liquid is distilled at the constant pressure P its boiling point rises. If $\frac{dP}{dx}$ remains positive as x diminishes to zero, pure A will ultimately be left in the distilling flask.

On the other hand, if $\frac{dP}{dx}$ is negative, we have by a similar calculation $\frac{p_b}{p_a} < x$. The residue then becomes richer in B, and the boiling point of the liquid rises until it becomes equal to the boiling point of pure B. During distillation under constant pressure the boiling point of the residue always rises to a constant maximum value (Konowalow).

Finally, if $x\frac{dP}{dx} = 0$ for any value of x, *i.e.* if the total vapour pressure curve has a maximum or a minimum, we have for this value of x the relationship $\frac{p_b}{p_a} = x$, *i.e.* the composition of the vapour is the same as the composition of the liquid. In this case the mixture distils at constant temperature without change in composition. A mixture containing 96 per cent. alcohol and 4 per cent. water is an example of this. Other examples are 20·2 per cent. aqueous hydrochloric acid and a 68 per cent. solution of nitric acid. These mixtures behave like chemical compounds (one-component systems), as they are capable of going from one phase to another without change in composition. (Ostwald uses the term hylotropic for this property.)

The concentration $x = \frac{p_b}{p_a}$ of the hylotropic mixture is, however, a function of the temperature, and hence also of the total pressure at which the mixture boils, as p_a and p_b are different functions of the temperature. This variation of composition

with pressure distinguishes hylotropic mixtures from true chemical compounds.

There are two distinct cases, according as the total pressure P is a maximum or a minimum at x_m. If P is a minimum, the total vapour pressure of any mixture of the two substances will increase at constant temperature during distillation, and ultimately become equal to the vapour pressure of one of the pure components (if the distillation is carried out at constant pressure, the temperature will rise until the boiling point of the pure component is reached). The residue is therefore either pure A or pure B. On the other hand, if $P_{x,\,m}$ is a maximum, distillation at constant pressure always results in a residue which has the composition corresponding to the maximum boiling point.

The first distillate from any mixture is always richer in the component which produces an increase in the total vapour pressure when added to the mixture. The first distillate has therefore always a higher vapour pressure and a lower boiling point than the residue. By repeated partial distillation at constant pressure (fractional distillation) we obtain ultimately the distillate of maximum vapour pressure and minimum boiling point. Thus, by fractional distillation of mixtures which have a maximum boiling point, we obtain ultimately a distillate consisting of the constant boiling point mixture. Mixtures of liquids which have a minimum vapour pressure yield one or other of the pure components. If the vapour pressure of the mixture lies between the minimum and P_a, pure A will be obtained, otherwise the distillate will consist of pure B. Fractional distillation of a mixture always results in a distillate consisting of the component or mixture of maximum vapour pressure and lowest boiling point, and in a residue consisting of the liquid of minimum vapour pressure and highest boiling point. Complete separation of both pure components by fractional distillation is only possible when the maximum and the minimum of the total vapour pressure curve coincide with the beginning and the end of the curve.

Mixtures of alcohol and water, for example, have a maximum vapour pressure. The product which is obtained on the large scale in the fractional distillation of alcohol is thus not pure alcohol, but a mixture containing 4 per cent. of water, which

can only be removed by means of chemical drying agents. The acids mentioned above, on the other hand, have minima. The following pairs of liquids have also a maximum: water and propyl alcohol, water and butyric acid, ethyl alcohol and chloroform, ethyl alcohol and benzene, acetone and carbon disulphide, etc. Water and sulphuric acid, aceton and chloroform, methyl alcohol and ethyl iodide, etc., have a minimum.

The following pairs have neither a maximum nor a minimum vapour pressure: water and acetone, ethyl alcohol and acetone, ethyl alcohol and carbon disulphide, acetic acid and benzene, ether and benzene, etc. The following pairs have rectilinear vapour pressure curves: benzene and chlorbenzene, benzene and brombenzene, toluene and chlorbenzene, ethylene bromide and propylene bromide. Thus, for very similar pairs, the vapour pressure curve is a straight line.

The Duhem-Margules equation (9 *et seq.*) was first confirmed quantitatively by v. Zawidzki.* Margules showed that from the relationships $$P = F(x) = p_a + p_b = f_1(x) + f_2(x)$$ general formulae for f_1 and f_2 can be deduced which satisfy the differential equation (9). When the total vapour pressure curve F has been determined by experiment, f_1 and f_2, and hence also p_a and p_b can be calculated for all values of x, and compared with experimental determinations of p_a and p_b. The calculations, which are not altogether easy, have been carried out by v. Zawidzki and found to be in satisfactory agreement with experiment. The agreement, however, can never be complete, as the calculation of the analytical expression for the function $P = F(x)$ from a few experimental figures always involves a certain amount of error. For this reason Bose devised a graphical method,† which, with careful drawing, gives very good results. The figures obtained from the total pressures by this method are in excellent agreement with the experimental determinations of p_a and p_b by v. Zawidzki.

Experimental determination of partial vapour pressures. The experimental determination of the partial pressures over a mix-

* *Zeitschr. f. physikal. Chemie*, **35**, 129 (1900).

† *Zeitschr. f. physikal. Chemie*, **8**, 353 (1907).

ture of liquids generally consists of a determination of the ratio $\frac{p_a}{p_b}$ in a small distillate from a large quantity of the mixture. The distillate is analysed either by determining the total pressure at which ebullition begins at a fixed temperature, or by measuring the boiling point at constant pressure. The accuracy of the method depends chiefly upon the completeness of the equilibrium between liquid and vapour during the distillation, and upon the accuracy of the analysis of the distillate. The analysis of a mixture of organic liquids generally consists of a determination of some physical constant of the mixture, such as the refractive index.

Perhaps the best results by this method will be found in v. Zawidzki's paper which we have already quoted several times, and in which the older literature on this subject is treated fairly completely. Recently Rosanoff and his colleagues have worked out a different method.* A gaseous mixture of the two components in a constant and definite ratio is passed through the liquid mixture, which may be of any concentration. If the composition of the gaseous mixture is not the same as that of the saturated vapour, the component present in excess will condense. This will cause the temperature of the liquid to rise. The change in concentration will not cease until vapour and liquid are in equilibrium, and the temperature has become constant. It is, therefore, only necessary to determine for a given total pressure the temperature corresponding to an arbitrarily chosen partial pressure ratio, and then by subsequent analysis to determine the composition of the liquid in equilibrium with the gaseous mixture.

Variation in the boiling point of liquid mixtures. The normal boiling point of a mixture of liquids is the temperature at which the total vapour pressure is equal to the atmospheric pressure. The difference in boiling point between the mixture and either of the pure components can be calculated by integrating the Nernst equation (8) (p. 235) between the boiling point of the component and the boiling point of the mixture. The calculation is similar to that by which the raising of the boiling point

* *Zeitschr. f. physikal. Chemie*, **66**, 349; **68**, 641 (1910).

of solutions of non-volatile substances was obtained (p. 230). We shall restrict the calculation in the first instance to the simple case in which the less volatile component B is present only in very small quantities, so that the mixture may be regarded as a very dilute solution of B in the more volatile solvent A. The calculation of the raising of the boiling point follows at once from Fig. 30 (cf. Fig. 25, p. 229).

P_a is the vapour pressure curve of the pure liquid A, p_a the partial vapour pressure curve, and P the total vapour pressure

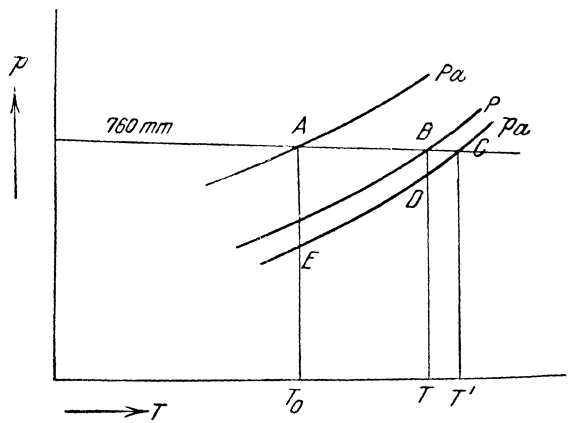


FIG. 30.

curve of the mixture. Thus T_0 is the boiling point of A and T the boiling point of the mixture (the solution). T' is the temperature at which the partial pressure of A in the solution is equal to the atmospheric pressure.

Hence we have

$$T - T_0 = AC - BC = (T' - T_0) - (T' - T),$$

and

$$\frac{AE}{AC} = \tan ACE = \frac{BD}{BC};$$

also $AE = (P_a - p_a)_{T_0}$, $BD = (P - p_a)_T = p_{b_T}$, $\tan ACE = \frac{dp_a}{dT}$,

and therefore

$$T - T_0 = \frac{(P_a - p_a)_{T_0} - p_{b_T}}{\frac{dp_a}{dT}} = -\frac{(P_a - p_a)_{T_0} - p_{b_T}}{p_{a_{T_0}} \cdot L_a} \cdot RT_0^2$$

(if the heat of evaporation L_a of the solvent is unaltered by the addition of a small amount of B, and if L_a remains constant between T_0 and T). This equation may be written in the form

$$T - T_0 = -\left(\left[\frac{P_a - p_a}{p_a}\right]_{T_0} \cdot \frac{RT_0^2}{L_a} - \frac{p_{b_T}}{p_{a_{T_0}}} \cdot \frac{RT_0^2}{L_a}\right) \ldots\ldots (10)$$

In order to calculate the change in boiling point it is therefore necessary to know the latent heat of the solvent, the relative lowering of the vapour pressure, and also the composition of the saturated vapour at T and T_0. The boiling point of the solution will be higher or lower than that of the pure solvent according as $(P_a - p_a)_{T_0} \gtrless p_{b_T}$.

Thus the boiling point of pyridine* is lowered by the addition of small quantities of water, while the boiling point of benzene or of alcohol is raised by the addition of iodine. In any case it is necessary to know the composition of the saturated vapour before determinations of the change in boiling point with concentration in solutions of volatile substances can be utilised in calculations. Suitable apparatus for this purpose have been devised by Beckmann and others.†

The change in the freezing point of substances which form solid solutions can be calculated in a similar manner. For the purposes of this calculation it is necessary to know the vapour pressures of the solid solvent and the partial pressures of the solid solution. It is easy to show that the freezing point of a solution of this kind may even be higher than that of the pure solvent, just as (by 10) the boiling point of a solution may be lower than that of the pure solvent. Actual cases in which the freezing point is raised have recently been observed by v. Hevesy‡ and Sackur.§

3. Saturated solutions.

A saturated solution in presence of its saturated vapour is a monovariant system (three phases and two components). A

* Wilcox, *Journ. Phys. Chem.* **14**, 576 (1910).

† *Zeitschr. f. physikal. Chemie*, **58**, 543 (1907).

‡ *Zeitschr. f. physikal. Chemie*, **73**, 677 (1910).

§ *Zeitschr. f. physikal. Chemie*, **78**, 550 (1912).

change in the temperature therefore produces not only a change in the vapour pressure, but also in the concentration of all phases of variable composition (all solutions which take part in the equilibrium). Here also the relation between the variations in concentration, pressure, and temperature is given by the Clausius equation.

We shall consider here only solutions of solid substances in which the concentration of the solute is vanishingly small.

If the saturated solution contains x mols of the solid solute in each mol of solvent, x mols of the solid will dissolve when 1 mol of the vapour condenses. In this process the total volume changes by $-(v_3-v_2+xv_1)$, where v_3 and v_1 are the molecular volumes of the vapour and the solid, and v_2 is the volume of the saturated solution which contains 1 mol of solvent and x mols of solute. At the same time, the quantity of heat $-(L-xL_l)$ will be evolved where $L(<0)$ is the heat of evaporation of the solvent, and $+L_l$ is the heat which is evolved when 1 mol of the solid solute is dissolved in the quantity of the solvent necessary to produce the saturated solution. The quantity of heat L_l is called the total or integral heat of solution.

Applying the Clausius equation, we have

$$\frac{dp}{dT}=\frac{-(L-xL_l)}{T(v_3-v_2+xv_1)}.$$

Neglecting the specific volumes of the solution and the solute in comparison with the specific volume of the saturated vapour, and assuming that the vapour obeys the gas laws, we have

$$\frac{dp}{dT}=\frac{-(L-xL_l)p}{RT^2},$$

or

$$\frac{d\,ln\,p}{dT}=-\frac{L}{RT^2}+x\frac{L_l}{RT^2}, \quad \text{.....(11)}$$

where p is the vapour pressure of the saturated solution. For the vapour pressure of the pure solvent, we have

$$\frac{d\,ln\,p_0}{dT}=\frac{-L}{RT^2},$$

and hence

$$\frac{d\,ln\,\frac{p}{p_0}}{dT}=+x\frac{L_l}{RT^2}. \quad \text{.....(11}a\text{)}$$

The relative lowering of the vapour pressure $\frac{p_0-p}{p_0}=1-\frac{p}{p_0}$ increases with the temperature when $L_l<0$, *i.e.* when heat is absorbed as the solid solute dissolves. On the other hand, if the total heat of solution $+L_l$ is positive, the relative lowering of the vapour pressure of the saturated solution diminishes as the temperature is raised.

L_l is negative for most solutions of solids, especially for aqueous solutions, so that the relative lowering of the vapour pressure generally increases with the temperature. When the solubility and the heat of solution are very large, the vapour pressure of the saturated solution may even diminish as the temperature is raised, for then the term $x\frac{L_l}{RT^2}$ in equation (11) becomes more strongly negative than $\frac{-L}{RT^2}$ is positive. This peculiar phenomenon (diminishing vapour pressure with rising temperature) has recently been observed by Speranski * in saturated aqueous solutions of sodium thiosulphate.

It is necessary to distinguish between the total heat of solution and two other kinds of heat of solution. The first of these is the heat evolved when 1 mol of the solute is dissolved in a very large volume of solvent so as to form a very dilute solution. This is generally spoken of simply as the "heat of solution." It is the easiest to determine experimentally, as solution proceeds so rapidly in the presence of a large amount of solvent, that the heat evolved can be measured in a calorimeter. Thus most of the published data, such, for example, as the numerous determinations of J. Thomsen, are given in terms of this heat of solution. It differs from the integral heat of solution by the heat evolved when the saturated solution is diluted indefinitely.

By the differential heat of solution is meant the heat which is evolved when 1 mol of the solute is dissolved in a very large quantity of the saturated solution. For very sparingly soluble substances whose saturated solutions may be regarded as infinitely dilute, the three kinds of heat of solution become identical.

* *Zeitschr. f. physikal. Chemie*, **78**, 86 (1911).

The differential heat of solution is of theoretical importance in the calculation of the variation of solubility with pressure. If a saturated solution containing solid solute is subjected to a pressure greater than the vapour pressure of the solution, the gaseous phase disappears and the system becomes divariant (two phases and two components). The concentration of the saturated solution (*i.e.* the solubility) is then a function of the pressure as well as of the temperature. When a "condensed" system of this kind is subjected to a further change in pressure the solid solute and the solution will not remain in equilibrium unless the temperature is changed simultaneously. As in the analogous case of the variation with pressure of the melting point of a pure substance (p. 221), the Clausius equation assumes the form

$$\frac{dp}{dT} = \frac{-L_l'}{T(v_2 - v_1)}.$$

Here L_l' is the amount of heat which is evolved when 1 mol of the solute is dissolved in the saturated solution (differential heat of solution). $v_2 - v_1$ is the change in volume which the solute undergoes in dissolving in the saturated solution, *i.e.* the difference between the molecular volumes in the solid and in the dissolved state. Thus a compression by dp, subject to the condition that the solubility remain constant, must be compensated by a raising or a lowering of the temperature according as the sign of $\frac{L_l'}{v_2 - v_1}$ is negative or positive.

The above equation is only valid for constant solubility, so that we must also have

$$dx = \frac{\partial x}{\partial p}\,dp + \frac{\partial x}{\partial T}\,dT = 0,$$

and hence

$$\frac{\partial x}{\partial p} = -\frac{\partial x}{\partial T} \cdot \frac{\partial T}{\partial p}.$$

Hence we obtain the equation

$$\frac{\partial x}{\partial p} = \frac{\partial x}{\partial T} \cdot \frac{T(v_2 - v_1)}{L_2'}$$

for the variation of the solubility with the pressure. This equation was first deduced in a slightly different form by

Braun,* who also showed that it was in qualitative agreement with experiment. The equation is of historical interest, as it was the starting point from which Braun arrived at the principle which is called after him and Le Chatelier (p. 207).

Thus, if heat is absorbed in the process of solution ($L_l' < 0$), the solubility at constant pressure increases as the temperature is raised $\left(\frac{\partial x}{\partial T} > 0\right)$. If solution is accompanied by contraction ($v_2 - v_1 < 0$), the solubility at constant temperature increases as the pressure is increased $\left(\frac{\partial x}{\partial p} > 0\right)$. We see that these, and also the converse propositions, are in accord with the above equation. Quantitative experiments in confirmation of the equation have not yet been carried out with success, as the accurate measurements necessary are exceedingly difficult to perform.†

4. An equation of condition for dilute solutions.

In deducing the equations (1) to (11) of the previous paragraph, in which relationships between the variables of condition of solutions (pressure, temperature, and composition) and their thermal properties (heat of solution, heat of dilution, etc.) are postulated, we have always assumed the validity of the gas laws for the gaseous phase. In doing so, we have exceeded the bounds of strict thermodynamical reasoning, and our results have no longer the exact validity of pure deductions from the laws of thermodynamics. By introducing this assumption, however, we have been able to integrate the differential equations of thermodynamics for certain ranges of temperature, and test them by experiment. In carrying out the integration, we neglected the volumes ‡ of the solid and liquid phases, which appear in the exact equations, in comparison with the volume of the gaseous phase, and expressed this latter volume as a function of pressure and temperature with the aid of the gas laws. The introduction of the gas laws enables us to reduce by one the number of the unknown functions which appear in

* Wiedemanns, *Annalen*, **30**, 250 (1887); *Zeitschr. f. physikal. Chemie*, **1**, 259.

† See also Sorby, *Proc. Roy. Soc.* **12**, 538 (1863). ‡ Molecular volumes.

the differential equations. In general, this procedure is justified by experiment, in so far at least as the temperatures considered are well below the critical points of the liquids concerned.

We may go a step further, however, and introduce an equation of condition for solutions, that is, an equation by which we can calculate the variables of condition of solutions from their composition (specific volumes or concentrations of the components). It is convenient to choose the variable which is easiest to determine experimentally as independent variable. For solutions this is generally their composition or concentration, *i.e.* the number of mols of solvent or solute in unit volume or in unit mass of the solution. In most cases the concentration can be determined directly by analysis. If c is the number of mols of the solute, and c_0 the number of mols of the solvent in unit volume (1 litre) of the solution, these two concentrations are connected by the equation $Mc + Mc_0 = 1000s$ where M and M_0 are the molecular weights of solute and solvent respectively, and s is the density of the solution. Hence only one of the two quantities c and c_0 can be taken as independent variable.

The equation of condition of a solution whose vapour pressure is p may then be written in the form $p = F(T, c)$. The analytical form of the function F can no more be deduced from purely thermodynamical considerations than the corresponding function for gases. The equation of condition must, therefore, either be taken directly from experiment (*e.g.* by determining p for different values of c and T, and expressing the results in the form of an equation), or by making an hypothesis as to the nature of the equation and testing its consequences by experiment. Both methods have been employed with success. They will be discussed in detail and compared with one another in the following.

As yet the equation of condition has been completely determined only for dilute solutions. The first general equation of the form $p = F(T, c)$, applicable to all solutions of any solute in any solvent, is due to Raoult.* Raoult's law states that the relative lowering of the vapour pressure of a solution (p. 228) of a

* *Zeitschr. f. physikal. Chemie*, **2**, 253; *Compt. rend. d. l'Acad. des Sc.* **104**, 1430 (1888).

practically non-volatile substance is independent of the chemical character of the solute and solvent, and is equal at all temperatures to the ratio of the molecules of the solute to the total number of molecules present (solvent+solute). If n molecules of the solute are dissolved in N molecules of the solvent, Raoult found that

$$\frac{p_0-p}{p_0}=\frac{n}{N+n}.$$

In unit volume $n=c$ and $N=c_0$, so that

$$\frac{p_0-p}{p_0}=\frac{c}{c_0+c}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

For very dilute solutions c is small compared with c_0, and we may, therefore, write $\frac{p_0-p}{p_0}=\frac{c}{c_0}$, where c_0 is the number of mols in unit volume of the solution. By a simple transformation, we obtain, from (1),

$$\frac{p}{p_0}=\frac{c_0}{c_0+c} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1a)$$

and

$$\frac{p_0-p}{p}=\frac{c}{c_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1b)$$

Raoult's law comprises four distinct statements, namely:

1. The relative lowering of the vapour pressure in solutions of any solute in any solvent is proportional to the concentration of the solute.

2. For the same temperature, and the same molecular concentration, solutions of different solutes in the same solvent have the same vapour pressure.

3. The relative lowering of the vapour pressure of solutions of the same concentration in different solvents is directly proportional to the molecular weight of the solvent, *i.e.* inversely proportional to the number of molecules of solvent in the solution.

4. The relative lowering of the vapour pressure is numerically equal to the ratio of the numbers of molecules of solute and solvent in the solution.

1 and 2 were proved in one or two cases by other authors before Raoult (*e.g.* Wüllner, see Ostwald, *Lehrb. d. allg. Chemie*, i. p. 705 *et seq.*). The numerical relationship to the number of

molecules of the solvent was, however, first recognised by Raoult.

Raoult established his law by a large number of determinations in which the nature of solvent and solute were varied widely. The most characteristic of his results for dilute solutions are given in the following tables. The law was found to hold good in all cases, except aqueous solutions of salts. We shall see later that the exceptions can be accounted for satisfactorily by the electrolytic dissociation theory.

Solute.	Solvent ether.	
	$\frac{n}{N+n}$	$\frac{p_0-p}{p_0}$
Turpentine	0·059	0·060
	0·121	0·119
Nitrobenzene	0·060	0·055
Aniline	0·0385	0·040
	0·077	0·077
Methyl salicylate	0·048	0·040
	0·092	0·084
Ethyl benzoate	0·049	0·051
	0·096	0·091

This table confirms the 1st, 2nd, and 4th parts of the law for ether. The differences between the 2nd and 3rd columns are not greater than might be expected with Raoult's primitive apparatus. The table on p. 253 shows that the relative lowering of the vapour pressure is independent of the chemical nature of the solvent. The last column contains the observed values of the relative lowering $\frac{p_0-p}{p_0}$ produced by the addition of 1 mol of solute to 100 mols of solvent. The figures are the mean values for a large number of different solutes.

If the law were strictly accurate, $\frac{p_0-p}{p}$ should always be equal to $\frac{1}{100+1}=0{\cdot}0099$. The measurements, which were carried out with solutions of about 4-5 mols. of the solutes in 100 mols. of the solvent, thus gave rather too high values for

the lowering of the vapour pressure. We are, however, justified in assuming that Raoult's law is strictly valid for very dilute solutions.*

Solvent.	Molecular weight.	$\frac{p_0 - p}{p_0}$.
Water - - - -	18	0·0102
Phosphorous trichloride	137·5	0·0108
Carbon disulphide -	76	0·0105
Carbon tetrachloride -	154	0·0105
Chloroform - - -	119·5	0·0109
Amylene - - -	70	0·0106
Benzene - - -	78	0·0106
Methyl iodide - -	142	0·0105
Ethyl bromide - -	109	0·0109
Ether - - - -	74	0·0096
Acetone - - -	58	0·0101
Methyl alcohol - -	32	0·0103

Raoult's experiments were performed in the following manner. Two barometer tubes at the same temperature were placed side by side. A portion of the solvent was introduced into one and a portion of the solution into the other. The difference in level of the mercury columns was then measured (cf. Fig. 11, p. 52). The temperature was chosen so that the vapour pressure of the pure solvent was always about 400 mm. The vapour pressure of the solute could always be neglected.

As will be shown in the following, the equations of the previous paragraph can be simplified considerably with the aid of Raoult's law.

(*a*) *Temperature and vapour pressure lowering.* By equation (3), p. 228, we have

$$\frac{d\, ln\, \frac{p}{p_0}}{dT} = -\frac{L - L_0}{RT^2},$$

and by (1*a*), p. 251,

$$\frac{p}{p_0} = \frac{c_0}{c_0 + c},$$

* R. Maier has recently found Raoult's law to hold with great accuracy for solutions of cane-sugar in water at 0° for concentrations up to 1*n*. (*Ann. d. Physik*, **31**, 423 (1910)).

i.e. independent of the temperature.* Hence the heat of dilution $L - L_0 = L_v$ is zero.

Raoult's law can therefore only be true for solutions in which no heat is evolved on further dilution. This is a necessary but not a sufficient condition for the validity of Raoult's law.

(*b*) *Raising of the boiling point.* Equation (4), p. 230, states that

$$T - T_0 = -\frac{RT^2}{L_0} \cdot \frac{p_0 - p}{p_0} = -\frac{RT^2 c}{L_0 c_0} = -\frac{RT^2 c}{L'}.$$

In dilute solutions $L_0 c_0 = L'$ is the heat of evaporation for unit volume (1 litre) of the solvent. The raising of the boiling point is therefore proportional to the molal concentration of the solute. The quantity $\frac{T - T_0}{c}$, *i.e.* the molecular raising of the boiling point, can be calculated from the boiling point and the heat of evaporation of the solvent. This equation was first deduced by van't Hoff for the lowering of the freezing point, and was then applied by Arrhenius to the raising of the boiling point. It has been confirmed experimentally by Beckmann and others in a large number of cases.

If the concentration is reckoned in mols. per kilo. (according to Raoult) instead of in mols. per litre (according to Arrhenius), then L' is the latent heat of 1 kilo. of solvent. Table A contains a selection from the available experimental data in confirmation of this law (Landolt and Börnstein, 3rd edition).

(*c*) *Lowering of the freezing point.* Equation (6), p. 231,

$$T_0 - T = -\frac{RT_0^2}{W} \cdot \frac{p_0 - p}{p},$$

becomes

$$T_0 - T = -\frac{RT_0^2}{Wc_0} c = -\frac{RT_0^2 c}{W'},$$

which is analogous to the equation for the raising of the boiling point, and differs from it only in that the heat of fusion and the freezing point appear in place of the heat of evaporation and the boiling point (van't Hoff). The validity of this equation is shown by Table B, which also is a selection from the large number of data available.

* This involves the assumption, however, that the ratio $\frac{c}{c_0}$ is not altered by the thermal expansion.

TABLE A.

I. Proportionality between raising of the boiling point and concentration.

Solvent.	T_0° C.	Solute.	c mols. in 1 kg.	$T - T_0$.	$\frac{T - T_0}{c}$.	$\frac{RT_0^2}{L'}$.
Water*	100	Mannitol	0·131	0·065	0·50	$\frac{2 \times 373^2}{532000} = 0{\cdot}52$
			0·256	0·121	0·51	
			0·696	0·360	0·52	
,,	100	Cane sugar	0·126	0·064	0·51	
			0·322	0·164	0·51	
			0·634	0·317	0·50	
Ethyl Alcohol†	78·8	Mercuric chloride	0·108	0·126	1·17	$\frac{2 \times 352^2}{206000} = 1{\cdot}2$
			0·219	0·259	1·18	
			0·85	1·010	1·18	
			1·14	1·345	1·15	
,,		Urea	0·022	0 024	1·11	
			0·041	0·044	1·07	
			0·044	0·048	1·09	
Benzene	80·3	Anthracene	0·067	0·169	2·52	$\frac{2 \times 353^2}{93000} = 2{\cdot}68$
			0·136	0·353	2·58	
			0·158	0·408	2·60	
,,		Benzil	0·066	0·171	2·60	
			0·134	0·336	2·51	
			0·191	0·471	2·47	

II. Molecular raising of the boiling point and heat of evaporation in dilute solutions.*

Solvent.	T_0° C.	Heat of evaporation per gram.	$\frac{T - T_0}{c}$.	
			Found.	Calculated.
Bromine	+63	43·7	5·2	5·2
Ammonia	−33·7	336·5	3·2	3·4
Sulphur dioxide	−10	91·8	1·50	1·49
Carbon disulphide	+46·2	86·7	2·37	2·35
Chloroform	61·2	58·5	3·66	3·82
Nitroethan	114	92·0	2·60	3·31
Ethyl ether	35·0	90·45	2·11	2·10
Acetone	56·3	125·3	1·725	1·73
Pyridine	115	104	2·95	2·90
Ethyl acetate	74·6	92·7	2·61	2·61

* Landolt-Bornstein, 3rd edition.

† Beckmann, *Zeitschr. f. physikal. Chemie*, **6**, 437 (1890).

TABLE B.

I. Proportionality between freezing-point depression and concentration.

Solvent.	T_0° C.	Solute.	c mols. in 1 kg.	$T - T_0$.	$\frac{T_0 - T}{c}$.	$\frac{RT^2}{W'}$.
Water*	0	Glycerine	0·0200	0·0372	1·86	$\frac{2 \times 273^2}{80000} = 1{\cdot}86$
			0·1008	0·1869	1·86	
			0·2031	0·3758	1·85	
		Chloral hydrate	0·0201	0·0373	1·86	
			0·1009	0·1875	1·86	
			0·4143	0·7685	1·855	
			1·135	2·117	1·864	
		Urea	0·00107	0·001983	1·85	
			0·00414	0·007668	1·85	
			0·01869	0·03463	1·85	
		Cane sugar	0·000332	0·000631	1·90	
			0·001410	0·00264	1·87	
			0·009978	0·01856	1·86	
			0·0201	0·0378	1·86	
Phenol †	38·5	Naphthalene	0·080	0·64	8·0	$\frac{2 \times 311{\cdot}5^2}{25500} = 7{\cdot}6$
			0·160	1·285	8·0	
			0·320	2·525	7·9	
			0·64	4·825	7·6	
Naphthylamine †	47·12	Camphor	0·053	0·415	7·85	$\frac{2 \times 320^2}{25600} = 8{\cdot}0$
			0·106	0·845	7·95	
			0·212	1·73	8·2	
			0·424	3·49	8·2	
			0·689	5·72	8·3	

* Landolt-Börnstein, 3rd edition.

† Eykmann, *Zeitschr. f. physik. Chemie*, **3**, 203 (1888).

II. Molecular freezing-point depression and latent heat of fusion of dilute solutions.

Solvent.	T_0° C.	Heat of fusion per gram.	$\frac{T-T_0}{c}$. Found.	$\frac{T-T_0}{c}$. Calculated.
Phosphorus	44	5·034	39	39·9
Nitrogen peroxide	−10·95	37·2	4·1	3·99
Stannic bromide	+26·4	7·07	24·3	26·0
Sulphuric acid monohydrate	8·4	31·72	4·8	5·0
Fused potassium chloride*	772	86	25	25·3
Fused calcium chloride*	765	54·6	42	39·4
Formic acid	8	57·4	2·8	2·75
Acetic acid	17	43·7	3·9	3·85
Benzene	5·5	29·4	5·12	5·27
Nitrobenzene	5·3	22·3	7·05	7·0
p-Toluidine	39·1	39·0	5·3	5·1
o-Nitrophenol	44·3	26·8	7·44	7·5
p-Dibrom benzene	87	20·6	12·4	12·6

(*d*) *Solutions of gases and liquids.* The validity of Raoult's law for a component A implies a linear relationship between the partial pressure of A and the mol fraction.

On page 233 we wrote

$$x=\frac{c}{c_0} \quad \text{and} \quad \frac{1}{1+x}=\nu_a=\frac{c_0}{c_0+c}.$$

Thus, if

$$\frac{P_a-p_a}{P_a}=\frac{c}{c_0+c},$$

we have

$$p_a=\nu_a P_a.$$

Hence, by (9), p. 237, it follows that $p_b=(1-\nu_a)P_b$, *i.e.* the vapour pressure of the second component is also a linear function of the mol fraction, and therefore likewise obeys Raoult's law (see p. 238). By (8), p. 235, we have again the necessary but not sufficient condition that the heat of mixture of the liquids be zero.

* Sackur, *Z. f. physikal. Chemie*, **78**, 550 (1912).

We can deduce an important result, as to the solubility of gases in liquids, from this theorem. A solution of this kind can be regarded as a liquid mixture of two substances A and B, in which the partial pressure p_b is the pressure of the dissolved gas over the liquid. Hence, if Raoult's law holds, we have

$$\frac{p_a}{P_a} = \frac{c_0}{c_0 + c} = \nu_a$$

and

$$\frac{d\ ln\ p_a}{d\nu_a} = \frac{1}{\nu_a},$$

and therefore, by (9f), p. 238,

$$\frac{d\ ln\ p_b}{d\nu_a} = -(1-\nu_a),$$

$$ln\ p_b = ln\ (1-\nu_a) + \text{const.},$$

$$p_b = k(1-\nu_a) = \frac{kc}{c_0 + c},$$

and for very dilute solutions

$$c = \frac{c_0}{k} \cdot p_b = \alpha \,.\, p_b.$$

This equation is known as Henry's law, and states that the solubility of a gas in a liquid is proportional to the partial pressure of the gas above the liquid. The constant α is called the coefficient of absorption. The law only holds for very dilute solutions, as is clear from the method by which it was derived.*

(*e*) *Boiling point of mixtures of liquids.* Equation (10), p. 245, states that

$$T - T_0 = -\left(\left[\frac{P_a - p_a}{p_a}\right]_{T_0} \cdot \frac{RT_0^2}{L_a} - \frac{p_{b\,T}}{p_{a\,T_0}} \frac{RT^2}{L_a}\right).$$

*It is not permissible to express the constant of integration k in terms of the pressure P_b, which the gas would exert if it could be obtained in the liquid state at the temperature of the experiment. Dolczalek (*Zeitschr. f. physikal. Chemie*, **71**, 206, 1910) falls into this error. Apart from the uncertainty of the extrapolation by which this pressure must be calculated when the temperature of the solution is above the critical temperature of the dissolved gas, it is also quite inadmissible to apply Margules' equation to vapours which do not obey the gas laws.

By Raoult's law, we have

$$\frac{P_a - p_a}{p_a} = \frac{c}{c_0}, \quad \frac{p_b}{p_a} = \frac{(1-\nu_a)P_b}{\nu_a P_a} = \frac{c}{c_0} \cdot \frac{P_b}{P_a},$$

and hence

$$T - T_0^* = -\frac{RT_0^2}{L_a'} \cdot c\left(\frac{P_a - P_b}{P_a}\right).$$

Thus the change in boiling point can again be calculated from the concentration of the solute, the molecular raising of the boiling point of the pure solvent $\left(\frac{RT_0^2}{L_a'}\right)$, and the vapour pressure P_b of the solute at the boiling point of the solvent. If $P_b > P_a$, the boiling point will be lowered, since L_a' is always negative.

As the change in boiling point is generally small in dilute solutions, few determinations are available for testing this equation. We can show, however, that the experiments of Rosanoff and Easley † on the boiling point of mixtures of benzene and ethylene chloride are in agreement with the theory.‡

In the table the molecular raising of the boiling point for benzene $-\frac{RT_0^2}{L_a'}$ has been taken as 2·67°, and in our notation $C_6H_6 = A$ and $C_2H_4Cl_2 = B$.

Boiling point.	ν_a.	Mols. $C_2H_4Cl_2$ in 1 kg. C_6H_6.	$\frac{T - T_0}{2{\cdot}67 \times c} = \frac{P_a - P_b}{P_a}$.
80·24	1	0	—
80·55	0·880	1·625	0·0715
80·90	0·776	3·44	0·0719
81·41	0·634	6·77	0·0647

For the two most dilute solutions, the expression $\frac{P_a - P_b}{P_a}$ is constant, that is to say, the approximations used in the derivation are permissible. From $\frac{P_a - P_b}{P_a} = 0{\cdot}072$ we find for the vapour pressure of pure ethylene chloride at the boiling point ($P_a = 760$ mm.) of benzene, $P_b = 760 \times 0{\cdot}928 = 706$ mm.

* For small values of $T - T_0$.

† *Zeitschr. f. physikal. Chemie*, **68**, 675 (1909).

‡ Zawidzki showed that mixtures of these liquids obey Raoult's law.

Staedel's determination * of the same quanfity at 80·25° gives approximately 680 mm. The agreement is very satisfactory, considering that determinations of the vapour pressure of the same substance by different investigators often differ by several per cent.

(*f*) *Solubility.* Equation (11*a*), p. 246, viz.

$$\frac{d\,ln\,\frac{p}{p_0}}{dT} = +x\frac{L_l}{RT^2},$$

combined with $x=\frac{c}{c_0}$ and $\frac{p}{p_0}=\frac{c}{c_0+c}$,

transforms into $$\frac{d\,ln\,\frac{c_0}{c_0+c}}{dT} = +\frac{c}{c_0}\frac{L_l}{RT^2}.$$

This transformation is only justifiable for very dilute solutions, *i.e.* when c is very small compared with c_0. We have then

$$ln\,\frac{c_0}{c_0+c} = -\frac{c}{c_0}$$

and $$\frac{dc_0}{dT}=0,$$

and hence $$\frac{d\,ln\,c}{dT} = -\frac{L_l}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (11')$$

The solubility therefore increases with the temperature when $L_l < 0$, *i.e.* when heat is absorbed in the process of solution. This relationship was discovered nearly simultaneously by Le Chatelier and van't Hoff. It is important to remember that the equation is only valid when Raoult's law holds, *i.e.* for solutions of sparingly soluble substances which do not conduct the electric current If the solute splits up into ions in solution, equation (11') must be modified accordingly. This law has been confirmed experimentally by various investigators, but almost exclusively for solutions of electrolytes.

* Winkelmann's *Handb. d. Physik,* iii. p. 1060.

5. Osmotic pressure.

As every solution of a non-volatile substance has a lower vapour pressure p than the pure solvent at the same temperature (p_0), there must be a diminution in free energy or an increase in entropy when a solution is diluted isothermally with an indefinite amount of the pure solvent. This diminution in free energy can be calculated, as it is equal to the maximum work obtainable in the isothermal dilution of the solution. For the purposes of this calculation it is only necessary to determine the work done when the dilution is carried out in any reversible and isothermal manner.

Helmholtz calculated the work done in the isothermal distillation of the solvent into the solution.* The reversible dilution by dv of any solution containing in the volume v 1 mol. of solute and x mols. of solvent can be performed as follows. The quantity of pure solvent (dx mols.) which, when mixed with the solution, increases its volume by dv, is evaporated reversibly and isothermally at the temperature T and the vapour pressure p_0. The vapour is then allowed to expand until its pressure has become equal to the lower vapour pressure p of the solution, and is then condensed so as to dilute the solution by dv. The quantities of work done in the evaporation and in the condensation are practically equal to one another, provided that the saturated vapour obeys the gas laws, and provided that the volume of the liquid is negligible compared with the volume of the vapour. Hence the total work done dw is equal to the work done by the vapour in expanding from p_0 to p.

Thus
$$dw = dxRT \ln \frac{p_0}{p}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$
if vapour and liquid are both composed of the same molecules. If this were not the case, for example, if the liquid were associated, dx would signify the number of mols. of vapour which on condensation would increase the volume of the solution by dv.

The same quantity of work can be obtained reversibly in another manner (van't Hoff). When a layer of pure solvent and a layer of solution are left in contact with one another, we observe in course of time that the solute migrates into the solvent

* See also Dieterici, *Ann. d. Physik* (3), **50**, 47 (1893).

layer. This motion of the solute can proceed against gravity, and does not cease until the solute is uniformly distributed throughout the whole of the available space (*i.e.* the solvent), or, in other words, until the liquid has the same concentration at all points. This process, which is similar to the expansion of a gas into a vacuum, is called the diffusion of the solute.

The tendency of the solute to become more dilute, which may be regarded as the force causing diffusion, can be made to do work. If we separate the solution from the solvent by a movable piston (as in Fig. 31), which permits the solvent but not the solute to pass through, this "semipermeable" piston will be forced upwards. The work done in this process is greater, the greater the pressure which has to be overcome in moving the piston, and reaches a maximum in the limiting case when the pressure on the piston is just sufficient to counterbalance the forces tending to cause the dilution. The motion of the piston is then infinitely slow, and the dilution of the solution takes place reversibly, so that the work done is a maximum. This limiting pressure is called the "osmotic pressure" (π) of the solution.

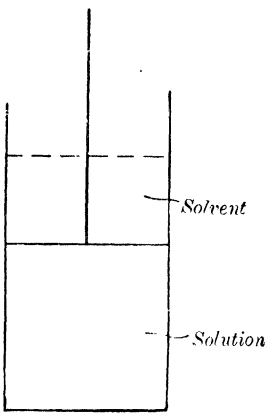


FIG. 31.

By this definition the osmotic pressure is dependent on the total pressure P on the solvent with which the solution is diluted. Fig. 32 will make this clear.* The solution is to the left of the semipermeable membrane A, the solvent to the right. Both solvent and solution are shut in by movable pistons. The membrane A will be in equilibrium when the pressure on the left-hand piston is greater by π than the pressure on the right-hand piston. Thus, if the former pressure is P, the latter is $P+\pi$. Let the volume of the solution be increased reversibly by dv,

* See Planck, *Zeitschr. f. physikal. Chemie*, **42**, 585; Duhem, *Mécanique Chimique*, **3**, 64.

while the volume of the pure solvent is diminished by the amount dv_0, which, on mixing with the solution, produces in it an increase in volume of dv. This can be done reversibly by moving the pistons so that the required amount of solvent is forced through the membrane from right to left. In this process the work done on the right-hand piston is $p\,dv_0$, and the work done by the left-hand piston is $(P+\pi)dv$. Thus the total work obtained is

$$dw' = \pi\,dv - P(dv_0 - dv) = \pi\,dv - P\,d\phi,$$

where $d\phi$ is the change in volume produced by the dilution.

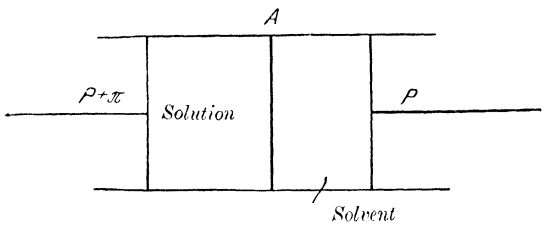


FIG. 32.

Unless the pressure P is very great, we may neglect $P\,d\phi$ in comparison with $\pi\,dv$. This is permissible when the solvent is subjected only to its own vapour pressure or to the pressure of the atmosphere. We have then

$$dw' = \pi\,dv. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

This equation applies to the dilution of a solution which is under the pressure $p+\pi$.

If we wish to calculate the work done dw in diluting the solution by dv under its own vapour pressure p, we must allow for the compression from p to $p+\pi$ before the dilution, and for the expansion to the pressure p after the dilution. The work done in these two operations is $\Pi\,dv$, where Π is the work which is necessary for the compression of unit volume of the solution from p to π. Hence

$$dw = dw' + \Pi\,dv.$$

But $$\Pi = \int_p^\pi p\,dv = \int_p^\pi \kappa \,.\, p\,dp = \frac{\kappa}{2}(\pi^2 - p^2),$$

where $\kappa = \frac{dv}{dp}$, the compressibility of the solution, is taken as a first approximation to be independent of the pressure. As p^2 is generally negligible compared with π^2, we obtain ultimately

$$dw = \pi\, dv + \frac{\kappa}{2}\pi^2\, dv. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Combining (1) and (3), we obtain

$$\frac{\kappa}{2}\pi^2 + \pi = \frac{dx}{dv} RT \ln \frac{p}{p_0}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

κ is generally very small, so that $\frac{\kappa}{2}\pi^2$ can be neglected in comparison with π unless π is very great. Thus, for water,

$$\kappa = 4{\cdot}5 \times 10^{-5}$$

for 1 atmosphere, so that even for an osmotic pressure 1 has to be greater, atmospheres $\frac{\kappa}{2}\pi^2 = 0{\cdot}225$, viz. only $\frac{1}{4}$ per cent. of π. For dilute, and for moderately concentrated solutions we have therefore

$$\pi = \frac{dx}{dv} RT \ln \frac{p_0}{p}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4a)$$

For formulae applicable to concentrated solutions, see Porter, *Proc. Roy. Soc.* **79**, 519; **80**, 457 (1908); Lord Berkeley and Hartley, *Phil. Trans. Roy. Soc.* **209**, 177 (1909); Callendar, *Zeitschr. f. physikal. Chemie*, **63**, 641 (1908).

The osmotic pressure of a solution can thus be calculated from the vapour pressures of the solvent and of the solution.

Equation (4*a*) is very approximately true if the saturated vapour obeys the gas laws. It is independent of all assumptions as to the nature of the relationship between the osmotic pressure and the concentration of the solution.

If we wish to express the osmotic pressure in atmospheres, we must take $R = 0{\cdot}082$ litre-atmospheres.

The quantity $\frac{dx}{dv}$ can be expressed in terms of quantities which can be determined by experiment. Let s be the specific gravity of a solution of which the volume v (litres) contains 1 mol. of

solvent and x mols. of solute. Also let M and M_0 be the molecular weights of solute and solvent respectively.

Then $$\frac{M+xM_0}{v}=1000\times s,$$

and hence $$dx=\frac{1000}{M_0}(s\,dv+v\,ds),$$

or $$\frac{dx}{dv}=\frac{1000}{M_0}\left(s+v\cdot\frac{ds}{dv}\right).$$

If c is the molal concentration of the solute (mols. per litre), then $c=\frac{1}{v}$, and we have

$$\frac{dx}{dv}=\frac{1000}{M_0}\left(s-c\frac{ds}{dc}\right).$$

Hence the osmotic pressure is given by the equation

$$\pi=\frac{1000}{M_0}\left(s-c\frac{ds}{dc}\right).RT\,ln\frac{p_0}{p}. \quad \text{.....(4b)}$$

For very dilute solutions $c=0$ and $s=s_0$, the specific gravity of the solvent. In this case we have (van't Hoff)

$$\pi=\frac{1000}{M_0}s_0RT\,ln\frac{p_0}{p}. \quad \text{.....(4c)}$$

In concentrated solutions, however, $s-c\frac{ds}{dc}$ is not equal to s_0, and the osmotic pressure can be calculated from the vapour pressure only when the density and the variation of the density with concentration have been determined experimentally.

The experiments of Lord Berkeley and Hartley with solutions of calcium ferrocyanide are in excellent agreement with equation (4*b*). So far as the author is aware, they are the only investigators who have simultaneously determined the osmotic pressure, the lowering of the vapour pressure, and the density of solutions of varying concentration, thus obtaining all the data necessary for an accurate test of equation (4*b*). The results are given in the following table. The values of $\pi_{calc.}$ were derived by the author from equation (4*b*). They represent the experimental data nearly as well as the values which Berkeley and Hartley

obtained by means of a much more complicated equation, in which they made allowance for the compressibility.

VAPOUR PRESSURE AND OSMOTIC PRESSURE OF SOLUTIONS OF CALCIUM FERROCYANIDE AT 0° C.

Gr. $Ca_2Fe(CN)_6$ in 1000 gr. H_2O.	s.	Mols. per litre c.	$\frac{ds}{dc}$.	$\frac{p_0}{p}$ (found).	$\pi_{calc.}$	$\pi_{found.}$
499·7	1·322	1·51	0·181	1·107	131 atm.	130·66 atm.
472·2	1·309	1·44	0·183	1·092	114 „	112·84 „
428·9	1·287	1·32	0·190	1·070	86·2 „	87·09 „
395·0	1·270	1·23	0·195	1·057	70·8 „	70·84 „
313·9	1·224	1·00	—	1·033	40·7 „	41·22 „

Equation (4*b*) becomes identical with (4*c*), even for concentrated solutions, when the specific gravity of the solution is a linear function of the concentration c, for then we have

$$s = s_0 + kc \quad \text{and} \quad \frac{ds}{dc} = k,$$

and hence

$$s - c\frac{ds}{dc} = s_0.$$

Equation (4*c*) is in most cases a good approximation to the truth, as the relationship between density and concentration in moderately concentrated solutions is at least approximately linear.

From equation (4*c*) we can derive an important consequence regarding the variation of the osmotic pressure with the temperature. On p. 229 $ln\frac{p_0}{p}$ was shown to be independent of the temperature when the heat of dilution of the solution is zero. In this case, if we neglect the variation of s_0 with the temperature, the osmotic pressure, like the pressure of a perfect gas, is proportional to the absolute temperature,

$$\pi = C \,.\, T. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

C is a function of the concentration, and also of the chemical character of solvent and solute. The nature of this function cannot be derived from pure thermodynamics.

Equation (5) is valid only when the heat of dilution is zero, and this, as we know from experiment, is only the case in very dilute solutions. It follows from equation (3), p. 228, that the osmotic pressure increases more rapidly than CT when the heat of dilution is negative. If heat is evolved on diluting the solution, the osmotic pressure increases more slowly than CT.

For very dilute solutions the relationship between the osmotic pressure and the vapour pressure can be deduced by another method, which is due to Arrhenius. Pfeffer's method of measuring the osmotic pressure of a solution is as follows:

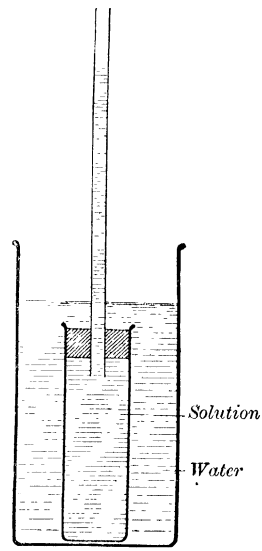


FIG. 33.

A porous clay pot is filled with an aqueous solution of potassium ferrocyanide and dipped into a solution of copper sulphate. The two solutions meet inside the porous wall of the pot and interact, forming an insoluble precipitate of copper ferrocyanide. A porous pot impregnated with copper ferrocyanide in this way acts as a semipermeable membrane which permits water but not dissolved substances to pass through it. If the pot be filled with an aqueous solution, and closed with a tight-fitting stopper furnished with an open glass tube (Fig. 33), and be then immersed in a beaker of pure water, the water will penetrate into the interior of the porous pot, and the liquid will rise in the glass tube until the hydrostatic pressure counterbalances the tendency of the solute to become more dilute, and prevents the further penetration of the solvent. The pressure of the column of liquid is then equal to the osmotic pressure of the solution. The first quantitative measurements of osmotic pressure were made by Pfeffer in this way with solutions of cane sugar.

Let h be the height of the column and s the specific gravity of the solution. The osmotic pressure is equal to the weight of

a column of liquid of height h and 1 sq. cm. cross-section, *i.e.*

$$\pi = hgs, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where g is the constant of gravity.

The vapour pressure p of the solution, at the surface of the solution in the glass tube, is equal to the vapour pressure of the pure solvent diminished by the pressure of a column of vapour of height h.* If this were not so, vapour would either distil from the surface of the liquid in the glass tube to the pure solvent below or, *vice versa*, from the solvent upwards to the surface of the solution. When osmotic equilibrium has been established, a distillation of this kind can no longer take place, and hence

$$p = p_0 - hgd. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The density d of the vapour (weight of 1 c.c.) can be calculated from the gas laws. We have

$$d = \frac{p_0 M_0}{1000 \,.\, RT},$$

where M_0 is the molecular weight of the vapour.

Hence, since $hg = \frac{\pi}{s}$ (by 6 and 7), it follows that

$$hgd = \frac{\pi}{s} \cdot \frac{p_0 M_0}{1000 \,.\, RT} = p_0 - p,$$

and

$$\pi = \frac{1000s}{M_0} \cdot RT \cdot \frac{p_0 - p}{p_0}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

For very dilute solution (4*c*) and (8) are identical, for we have then

$$\frac{p_0 - p}{p_0} = ln \frac{p_0}{p}$$

and

$$s = s_0.$$

For concentrated solutions and high columns of liquid the above calculation is not permissible, as the density of the vapour in the column of height h is not constant, but diminishes in accordance with the barometric height formula. Moreover, the solution at the membrane is under a considerable hydrostatic

* Arrhenius, *Zeitschr. f. physikal. Chemie*, **3**, 115 (1889); Gouy and Chaperon, *Ann. d. Chim. et de Phys.* (6), **13**, 124 (1888).

pressure, while the pressure at the surface of the column is only equal to the vapour pressure of the solution.*

Equations (4) and (8) also apply to solutions of volatile substances. p is then the partial pressure of the component, regarded as solvent, whose addition to the solution is accompanied by the doing of osmotic work.

The equations of § 1 (p. 228 *et seq.*), relating the vapour pressure of the solution to the lowering of the freezing point and the raising of the boiling point, now enable us to calculate the osmotic pressure in terms of these quantities.

(1) Osmotic pressure and raising of the boiling point.

(*a*) *For dilute solutions.*

By equation (4), p. 230, we have

$$T - T_0 = -\frac{RT_0^2}{L_0}\frac{p_0 - p}{p_0},$$

and by equation (8), p. 268, we have at T_0,

$$\pi_{T_0} = \frac{1000 s_0}{M_0} \cdot RT_0 \cdot \frac{p_0 - p}{p_0},$$

and hence

$$\pi_{T_0} = \frac{-1000 s_0 \cdot L_0 \cdot (T - T_0)}{M_0 \cdot T_0}. \quad \ldots\ldots\ldots\ldots (9)$$

L_0 is the molecular heat of evaporation, so that

$$\frac{1000 s_0}{M_0} L_0 = L'$$

is the heat of evaporation per unit volume (1 litre) of the solvent.

In order to obtain the pressure in atmospheres, it is necessary to multiply the heat of evaporation, which is usually expressed in calories, by the caloric equivalent of the litre atmosphere, viz. 24·1 (see p. 99).

(*b*) *For moderately concentrated solutions.*

By equation (5), p. 230, we have

$$\frac{1}{T_0} - \frac{1}{T} = \frac{R}{L} ln\, p_{T_0},$$

* See Earl of Berkeley and Hartley, *Proc. Roy. Soc.* 77, 156 (1906), and more especially Spens, *ibidem*, 234.

and by equation (4c), p. 265, for the boiling point of the solvent,

$$\pi_{T_0} = \frac{-1000 s_0}{M_0} \cdot RT_0 \, ln \, p_{T_0}.$$

Hence

$$\pi_{T_0} = \frac{-1000 s_0}{M_0} L \cdot T_0 \left(\frac{1}{T_0} - \frac{1}{T}\right) = -\frac{1000 s_0}{M_0} \cdot \frac{L(T - T_0)}{T}. \quad (10)$$

(9) differs from (10) in that $L = L_0 - L_v$ is the heat of evaporation of the solution (mean value between T and T_0).

(2) Osmotic pressure and lowering of the freezing point.

(*a*) *For dilute solutions.*

(T_0 and T are the freezing points of solution and solvent, W is the molecular heat of fusion, and L_v the heat of dilution of the solution.)

By (6), p. 231, and (8), p. 268, we have, for dilute solutions,

$$\pi_{T_0} = \frac{-1000 s_0}{M_0} \cdot \frac{W}{T_0} \cdot (T_0 - T), \quad \ldots\ldots\ldots\ldots (11)$$

and for concentrated solutions, by (7), p. 232, and (4c), p. 265,

$$\pi_{T_0} = \frac{-1000 s_0 (W - L_v)}{M_0} \frac{T_0 - T}{T} \cdot \quad \ldots\ldots\ldots\ldots (12)$$

The following example will illustrate the application of equations (9) to (12) to numerical calculations. Let us calculate, by means of equations (9) and (11), the osmotic pressures at 100° and at 0° of aqueous solutions, whose boiling points are

$$100{\cdot}1°, \; 100{\cdot}5°, \; 101{\cdot}0°, \; 102{\cdot}0°,$$

and whose freezing points are

$$-0{\cdot}1°, \; -0{\cdot}2°, \; -1{\cdot}0°, \; -2{\cdot}0°.$$

The heat of evaporation of 1 c.c. of water at 100° is

$$\frac{s_0}{M_0} L_0 = -536 \text{ cal.},$$

and the heat of fusion is -80 cal. Hence, for

$T = 373{\cdot}1°$ abs.	$373{\cdot}5°$ abs.
$\pi_{373°} = \frac{536 \times 0{\cdot}1}{373} \times \frac{1000}{24{\cdot}1} = 6{\cdot}0$ atm.	29·8 atm.
$T = 374°$ abs.	375°
$\pi_{373°} = 59{\cdot}6$ atm.	119 atm.,

and correspondingly for the freezing points,

$T = 272{\cdot}9°$	$272{\cdot}8°$
$\pi_{273°} = \frac{80 \times 0{\cdot}1}{273} \times \frac{1000}{24{\cdot}1} = 1{\cdot}2$ atm.	2·4 atm.
$T = 272°$	271°
$\pi_{273°} = 12$ atm.	24 atm.

6. Van't Hoff's osmotic pressure laws.

Dilute solutions. As has already been stated (p. 266), the relationship between the osmotic pressure of a solution and the concentration and chemical character of solvent and solute cannot be derived from purely thermodynamical considerations. There are several ways of attaining this end. In the first instance, the variation of the osmotic pressure with the concentration can be determined experimentally, and the results embodied in an empirical equation of the form $p = f(c)$. Or we may deduce relationships from kinetic conceptions of the nature of solutions, in much the same way as the gas laws were deduced. Or, finally, we may deduce the osmotic pressure laws, with the aid of the thermodynamical equations of the previous paragraph, from empirical or theoretical researches on the vapour pressure of solutions. These methods all lead to the same result, that the osmotic pressure of dilute solutions obeys the same laws as the pressure of a perfect gas. In other words, the osmotic pressure of a substance in solution is equal to the pressure which the substance would exert in the form of a perfect gas occupying, at the same temperature, the volume of the solution.

The osmotic pressure of a dilute solution is therefore given by the equation

$$\pi = \frac{RT}{v} = RTc. \quad \text{.....(13)}$$

Here v is the volume of the solution which contains 1 mol. of solute and c is the number of mols. in unit volume (1 litre) of the solution. When R is expressed in litre-atmospheres ($R = 0{\cdot}082$), the equation gives the osmotic pressure π in atmospheres.

This simple law was first deduced in 1886 by van't Hoff * from the analogy between the dissolved and the gaseous states, and was confirmed by the experiments of Pfeffer on the osmotic pressures of solutions of cane sugar, and of de Vries on the plasmolysis of plant cells in various solutions. Subsequent experiments, based for the most part on van't Hoff's thermodynamical deductions, have completely established this simple theory (for dilute solutions at least).

From equation (13) we derive the following simple equations for the lowering of the vapour pressure, the raising of the boiling point, and the depression of the freezing point of a dilute solution.

From (8) and (13), we have

$$\pi = R \,.\, T \,.\, c = \frac{1000 s_0}{M_0} \cdot RT \cdot \frac{p_0 - p}{p_0}$$

or

$$\frac{p_0 - p}{p_0} = \frac{c \,.\, M_0}{1000 s_0}.$$

$\frac{1000 s_0}{M_0}$ is the number of mols. in unit volume of the solvent. In dilute solutions $\frac{1000 s_0}{M_0}$ is very nearly equal to the number of mols. of solvent in 1 litre of solution, that is, $= c_0$ (cf. p. 250), and hence

$$\frac{p_0 - p}{p_0} = \frac{c}{c_0}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Thus van't Hoff's law leads to Raoult's law that the relative lowering of the vapour pressure of a solution is independent of all chemical properties, and is determined only by the mol fraction of solute and solvent (p. 251).

For the boiling point T_0 of the solvent, we have, by (13) and (9), the equation

$$\pi_{T_0} = RT_0 c = -\frac{1000 s_0}{M_0} \frac{L_0}{T_0} (T - T_0)$$

or

$$T - T_0 = -\frac{M_0}{1000 s_0 L_0} RT_0^2 c = \frac{-RT_0^2 c}{L'}, \quad \ldots\ldots\ldots\ldots (15)$$

where L' is the heat of evaporation of unit volume (1 litre) of

* Ostw. *Klassiker der exakten Wissenschaften*, No. 110.

the solvent. Similarly for the depression of the freezing point from (11) and (13),

$$T_0 - T = \frac{-RT_0^2}{W'} \cdot c.$$

The raising of the boiling point and the lowering of the freezing point are therefore proportional to the molal concentration. The constant of proportionality can be calculated from the latent heat of evaporation or fusion, and from the boiling or freezing point of the solvent.

Equations (15) and (16) have already been deduced from Raoult's law (p. 254) and compared with the experimental data. Their validity proves the correctness of van't Hoff's law for the osmotic pressure of dilute solutions and the independence of the osmotic pressure of the chemical peculiarities of solvent and solute.

The osmotic pressure of mixtures of solutions. According to van't Hoff's theory, the osmotic pressure of a solution depends only on the number of the dissolved molecules and not on their nature. Hence the osmotic pressure of a solution containing several substances is equal to the sum of the osmotic pressures due to the substances individually. Thus Dalton's law of partial pressures applies also to solutions. The relative lowering of the vapour pressure, raising of the boiling point, and depression of the freezing point are likewise proportional to the total molal concentration of the solution. Quantities of this kind, which do not depend on the chemical nature, but only on the number of the molecules present, were termed " colligative " by Ostwald.

We can derive some further important results from van't Hoff's laws of osmotic pressure.

The partition law. When a solution of a substance in a solvent A is shaken with another solvent B, which is not miscible in all proportions with A, but is capable of dissolving appreciable quantities of the solute (*e.g.* an aqueous solution of iodine with chloroform), part of the solute will be taken up by the second solvent, *i.e.* there will be a partition of the solute between the two solvents. The concentrations to which this partition proceeds are in definite relationship to one another, *i.e.* the concentration c_a of the solute in the solvent A is a function of

its concentration c_b in the second solvent B, so that we may write $c_a = f(c_b)$.

This follows from the phase rule, for we have a three-component system (two solvents and one solute) in three phases (two solutions and vapour), and hence two degrees of freedom. When the temperature and one of the concentrations, say c_a, are given, the concentration c_b in the second solvent is uniquely determined. The function f can be calculated when the osmotic pressure law is known for both solvents.

Consider two pairs of solutions (of the same components), each in partition equilibrium, and let the concentrations of the solute in the first solvent A be c_a and $c_a + dc_a$, and in the second solvent c_b and $c_b + dc_b$. Let all the solutions be present in such large volumes that the addition or withdrawal of 1 mol. of the solute does not appreciably alter the concentrations.

Consider now the following reversible and isothermal cycle :

1. By means of a semipermeable membrane let 1 mol. of the solute be withdrawn from the solution c_a. If π_a is the osmotic pressure and $v_a = \frac{1}{c_a}$ the volume of the solute, the osmotic work done in this process is $w_1 = -\pi_a v_a$.

2. Compress the mol. of solute until its concentration is $c_a + dc_a$. The work done in this process is

$$w_2 = \pi_a \, dv_a.$$

3. Force the mol. of solute (through a semipermeable membrane) into the solution $c_a + dc_a$. Here

$$w_3 = (\pi_a + d\pi_a)(v_a - dv_a).$$

4. Withdraw 1 mol. of the solute from the solution $c_b + dc_b$. Here

$$w_4 = -(\pi_b + d\pi_b)(v_b - dv_b).$$

5. Expand the mol. of solute until its concentration is c_b. Here

$$w_5 = -\pi_b \, dv_b.$$

6. Force the mol. of solute (through a semipermeable membrane) into the solution c_b. Here

$$w_6 = \pi_b v_b.$$

All the solutions have now returned to their original condition, and hence, as the cycle is isothermal and reversible,

$$w_1 + w_2 + w_3 + w_4 + w_5 + w_6 = 0.$$

or

$$v_a \, d\pi_a = v_b \, d\pi_b.$$

Thus far our reasoning has been entirely thermodynamical, except for the assumption of the possibility of such operations with semipermeable membranes. Combining the above equation with van't Hoff's law $\pi = \frac{RT}{v}$, we have

$$-v_a \frac{RT}{v_a^2} \, dv_a = -v_b \frac{RT}{v_b^2} \, dv_b,$$

or

$$\frac{dv_a}{v_a} = \frac{dv_b}{v_b}.$$

Integrating this equation from v_a to v_{a_2} and from v_{b_1} to v_{b_2} (where the solutions v_a and v_b are in partition equilibrium throughout the range of integration), we obtain

$$ln \frac{v_{a_2}}{v_{a_1}} = ln \frac{v_{b_2}}{v_{b_1}},$$

or

$$\frac{v_{a_2}}{v_{b_2}} = \frac{v_{a_1}}{v_{b_1}},$$

or

$$\frac{c_{a_1}}{c_{b_1}} = \frac{c_{a_2}}{c_{b_2}} = k.$$

The ratio of the concentrations in equilibrium with one another is therefore a constant independent of the concentrations of the individual solutions. This partition law was first clearly enunciated and established by Nernst.

Apparent exceptions to the partition law occur when the solute has not the same molecular weight in both solvents. For example, if the solute is associated in the solvent B, so that the solute molecule in B is n times as large as in A, the osmotic pressure in solvent B has only $\frac{1}{n}$th of the value which it would have if the molecules were single, for the osmotic pressure depends

on the number and not on the magnitude of the molecules. In this case, we have

$$\pi_b = \frac{RT}{nv_b},$$

and hence

$$\frac{dv_a}{v_a} = \frac{1}{n}\frac{dv_b}{v_b},$$

$$ln\frac{v_{a_2}}{v_{a_1}} = \frac{1}{n}\, ln\frac{v_{b_2}}{v_{b_1}},$$

$$\frac{v_{a_1}}{\sqrt[n]{v_{b_1}}} = \frac{v_{a_2}}{\sqrt[n]{v_{b_2}}},$$

or

$$\frac{c_{a_1}{}^n}{c_{b_1}} = \frac{c_{a_2}{}^n}{c_{b_2}} = k.$$

Thus Nernst * found by experiments on the partition of benzoic acid between water and benzene that this acid forms double molecules in benzene. This is shown by the following table:

c_a (grams benzoic acid in 10 c.c. water).	c_b (grams benzoic acid in 10 c.c. benzene).	$\frac{c_a}{c_b}$.	$\frac{c_a{}^2}{c_b}$.
0·0156	0·242	0·062	0·00093
0·0195	0·412	0·048	0·00092
0·0289	0·970	0·030	0·00086

Solubility of gases. If we take another gas or a vacuum for the second solvent B, the partition law tells us how a soluble gas will be divided between the gaseous phase and its solution in the solvent A. As the concentration in the gaseous phase is proportional to the partial pressure p of the gas, we have the equation

$$c = ap.$$

The solubility of a gas is therefore proportional to its partial pressure. Henry discovered and established this law in the beginning of the nineteenth century. It is connected thermodynamically with van't Hoff's osmotic pressure laws, and is therefore strictly accurate only in dilute solutions, that is, for sparingly soluble gases (see p. 258).

Diffusion. As was stated on p. 262, the osmotic pressure is

* *Zeitschr. f. physikal. Chemie*, **8**, 110 (1891).

a measure of the tendency of the solute to dilute itself, that is to say, it is a measure of the forces which bring about the equalisation of the concentration when solutions of different concentrations are brought into contact. The migration of the solute into the pure solvent, or from a concentrated into a dilute solution, is called diffusion. The laws of diffusion can be deduced from the osmotic pressure laws.*

Let us consider a cylindrical column of liquid whose concentration diminishes in the direction of the x-axis (Fig. 34). Let c be the concentration at the left bounding surface of a small column of liquid of length dx and cross-section dq, and let the osmotic pressure at this surface be π. Let the concentration and osmotic pressure at the right bounding surface be $c-dc$ and $\pi-d\pi$. Then the osmotic force on the left boundary in the direction of the arrow is $\pi\,dq$, and on the right boundary $(\pi-d\pi)dq$.

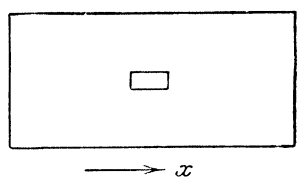


FIG. 34.

The element of volume is therefore subjected to the force $d\pi\,dq$ from left to right. As the motion of the solute in the liquid is retarded by a very large frictional resistance, the velocity of the solute will be proportional to the force, as in all cases where the friction is great. Hence, if the solute in this element of volume traverses the distance dx in the time dt, we have

$$\frac{dx}{dt}=k\,d\pi\,dq.$$

The quantity ds of the solute which crosses the boundary dq in the time dt is directly proportional to the time dt and inversely proportional to the length of the element of volume.

Hence
$$ds=k\frac{d\pi}{dx}\,.\,dq\,.\,dt.$$

Combining this with van't Hoff's law $\pi=RTc$, we have

$$ds=k\,.\,RT\frac{dc}{dx}\,.\,dq\,dt.$$

* Nernst, *Zeitschr. f. physikal. Chemie*, 2, 613 (1888); *Lehrbuch*, 6th edition, p. 157.

kRT depends only on the temperature and on the chemical nature of solvent and solute, and is independent of the concentration. Writing D for this quantity, we obtain

$$ds = D \cdot \frac{dc}{dx} \cdot dq \cdot dt.$$

This equation was deduced theoretically and confirmed experimentally by Fick in 1885, long before the discovery of the osmotic pressure laws. D is called the coefficient of diffusion.

7. The theoretical foundation of the laws of van't Hoff.

The discussions of the last paragraph show that a number of important properties of solutions can be deduced from the laws of osmotic pressure. Some of these have been known for a very long time, and all have been confirmed by experiment for dilute solutions. The deduction of these laws from the nature of the process of solution was therefore clearly a problem well worthy of solution. Van't Hoff's first attempt at an explanation was as follows.*

The tendency of the solute to dilute itself, which is measured by the osmotic pressure, is due to a force of attraction between the solute and the solvent. In dilute solutions each particle exerts the same force on the solvent, as it is uninfluenced by the neighbouring particles, and hence the total attraction is proportional to the number of the attracting particles, *i.e.* to the concentration of the solution.

As this line of reasoning only explains one of van't Hoff's laws, and is quite incapable of accounting for the identity of the osmotic pressure and the gaseous pressure, and also for the proportionality between the osmotic pressure and the temperature, it is clear that the assumption of forces of attraction is not a sufficient explanation. Later on van't Hoff himself laid stress on the analogy between the dissolved and the gaseous states, and explained osmotic pressure, in the same way as gaseous pressure, by the collisions of the solute molecules with the semipermeable membrane.† This kinetic conception of

* Published in his first paper before the Swedish Academy in 1885. Ostw. *Klassiker d. exakt. Wissensch.* No. 110, p. 12.

† *Zeitschr. f. physikal. Chemie*, **1**, 481 (1887). See also *Vorlesungen über theoretische Chemie*, **2**, 27.

osmotic pressure has been carefully studied and placed on a firm basis, for dilute solutions at least, by Boltzmann, Lorentz, Riecke,* and others. As van't Hoff points out, this explanation is clearly indicated by the fact that the osmotic pressure of solutions approaches zero as the temperature (and thermal motion) is diminished, whereas no reason can be adduced for the diminution of the attractive forces. On the other hand, this theory has been the object of several plausible and sometimes very violent attacks on the part of well-known investigators, which for the most part, however, have been shown to be due to misunderstanding.†

It is perhaps not yet possible to come to a conclusive decision on this important question. Kinetic conceptions have, however, proved so fruitful in all branches of physics and chemistry that we are justified in anticipating a similar success for the kinetic theory of solutions initiated by van't Hoff. As yet no other theory can compete with it in the services which it has rendered.‡

The validity of van't Hoff's laws for dilute solutions is not affected by the controversy on the possibility of explaining them. They have been completely established by experiment, not so much by direct measurements of osmotic pressure with semipermeable membranes as by the experimental confirmation of the thermodynamical consequences which have been derived from them. Thus all the deductions of the previous paragraph may be used conversely to confirm and to deduce the laws of van't Hoff. Van't Hoff himself used for this purpose one of the oldest and best known laws, namely, Henry's law of the absorption of gases by liquids, and showed that the equality of osmotic and gaseous pressure is a direct consequence of this law. His generalisation for solutions of other substances, although suggestive, is somewhat hypothetical in character. It is perhaps better, following the example of several other investigators, to take Raoult's law as the fundamental law for dilute solutions, and thence to deduce the laws of van't Hoff. We must not forget, however, that in doing so we are founding the

* *Zeitschr. f. physikal. Chemie*, **6**, 474, 564; **7**, 36, 88 (1891).

† Cf. Bredig, *Zeitschr. f. physikal. Chemie*, **4**, 447 (1889).

‡ Cf. O. Stern, *Dissertation*, Breslau, 1912.

theory of solution on a law which, although alluringly simple from a mathematical point of view, has not yet yielded to direct theoretical treatment, and which applies in the nature of things only to a limited number of solutions within certain definite limits of error.

The theory of electrolytic dissociation. Whereas the osmotic pressure and the other colligative properties of aqueous solutions of substances, such as cane sugar, obey van't Hoff's laws, marked deviations are met with in aqueous solutions of acids, bases, and salts, even at great dilutions. The osmotic pressure and lowering of the freezing point for these solutions are still found to be approximately proportional to the molecular concentration, but are considerably greater than the theoretical values. To allow for this van't Hoff introduced a new term into his osmotic pressure equation, writing for such solutions

$$\pi v = iRT.$$

For all monobasic acids (HCl), monoacid bases (NaOH), and their salts, i is nearly equal to 2, for dibasic acids and their salts approximately 3.

The factor i only occurs in solutions which are good conductors of electricity, and in 1887 Arrhenius succeeded in explaining these apparent deviations from the simple laws by his electrolytic dissociation theory. The molecules of an electrolyte are broken up to a greater or less extent into their free ions, even when the solution is not conducting a current of electricity. Thus we have the equation

$$HCl = H^{\cdot} + Cl',$$

where the positive charge of the cation is indicated by $^{\cdot}$, and the negative charge of the anion by $'$. These free ions have their own independent osmotic effect; in other words, they have the same tendency towards dilution as the electrically neutral molecules of the solute. The osmotic pressure of the solution is therefore the sum of the osmotic pressures of the two kinds of oppositely charged ions and of the osmotic pressure of the remaining undissociated molecules. Let α be the degree of dissociation, that is, the ratio of the molecules split up into free ions, to the total number of molecules in the solution. Then, if n ions result from the dissociation of one molecule, the number of ions pro-

duced by the dissociation of αc molecules is αnc. The total number of osmotically active molecules is then equal to the sum of the undissociated molecules and the free ions, *i.e.*

$$(1-\alpha)c+nc\alpha=c[1+(n-1)\alpha].$$

For monobasic acids and monoacid bases and their salts, we have $n=2$, and hence

$$\pi=RTc(1+\alpha),$$

and therefore $$i=1+\alpha.$$

Substances of this kind are called binary electrolytes. For dibasic acids and their alkali salts (ternary electrolytes), we have $n=3$, and therefore

$$\pi=RTc(1+2\alpha).$$

and hence $$i=1+2\alpha,$$

and so on.

The degree of dissociation α, which for very dilute solutions was found to be very nearly equal to 1, was calculated by Arrhenius from Kohlrausch's determinations of the electrolytic conductivity of the solution. From the data available at that time, Arrhenius was able to explain completely the anomalous behaviour of solutions of electrolytes. The table on p. 282 is taken from his first paper.*

Subsequent research has entirely confirmed the theory of Arrhenius. The chemical and electrochemical behaviour of solutions is closely connected with their ionic dissociation, and would be quite inexplicable without this theory. Rarely in the history of science has an idea proved so fruitful and suggestive, and led to the discovery of so many hitherto unsuspected relationships as this hypothesis of Arrhenius.

The further development of the theory of Arrhenius is not within the scope of this book. Let us conclude by pointing out, in emphatic contradiction of the views of certain authors to the contrary, that this theory has also rendered excellent service in explaining the behaviour of non-aqueous solutions. This has been proved by the recent work of Walden on this subject.

* *Zeitschr. f. physikal. Chemie*, **1**, 631 (1887).

Electrolyte.	i from the lowering of the freezing point.	i from the conductivity.
1. Bases.		
$Ba(OH)_2$	2·69	2·67
$S_2(OH)_2$	2·61	2·72
NaOH	1·96	1·88
KOH	1·91	1·93
NH_3	1·03	1·01
2. Acids.		
HCl	1·98	1·90
HNO_3	1·94	1·92
H_2SO_4	2·06	2·19
CH_3COOH	1·03	1·01
Malic acid	1·08	1·07
H_2S	1·04	1·00
3. Salts.		
KCl	1·82	1·86
NaCl	1·90	1·82
$NaNO_3$	1·82	1·82
K-acetate	1·86	1·83
Na_2CO_3	2·18	2·22
$BaCl_2$	2·63	2·54
$Ba(NO_3)_2$	2·19	2·13

(The figures refer to solutions containing 1 gram of the electrolyte in 1 litre of water.)

8. The theory of concentrated solutions.

Deviations from the simple laws. The exact proportionality between the osmotic pressure and the concentration can only hold in dilute solutions. No matter how we account for the osmotic pressure laws, whether by an attraction between the solvent and the solute, or by the impacts of the dissolved molecules, or whether we deduce them from the lowering of the vapour pressure of the solution, we are always forced to restrict the applicability of the simple laws of van't Hoff to the region of very dilute solutions. Similarly, the laws of perfect gases can only be regarded as valid in the limiting case of very great rarefaction. In concentrated solutions we must therefore expect

to find considerable deviations from the simple laws of solution, just as compressed gases differ in their behaviour from perfect gases. It is therefore an important object of research to demarcate the region of validity of the laws of van't Hoff, and to detect and find theories for the deviations from these laws.

In testing a proposed equation for the osmotic pressure of concentrated solutions, the comparison of the calculated values with the numerous experimental observations on colligative properties (p. 273), which are to be found in the literature of the subject, is often difficult on account of the fact that different authors express the concentrations of the solutions in different units. From the analogy between dilute solutions and gases it would appear rational to define the concentration of a solution as the number of mols. in unit volume (1 litre) of the solution. This system was adopted by Arrhenius. On the other hand, it is often simpler in experimental work to prepare a solution by weighing out the solute and the solvent, and to define the concentration accordingly (as in Raoult's papers), as the number of mols. of the solvent in unit mass (1 kilogr.) of the pure solvent. Writing c for the first kind of concentration, c' for the second, and s for the specific gravity of the solution, we have the equation

$$\frac{c'}{1000} = \frac{c}{1000s - Mc} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (a)$$

In very dilute solutions $s = s_0$ and Mc is small compared with $1000s$, so that $c = c's_0$.

In dilute aqueous solutions ($s_0 = 1$) the two concentrations become identical. In concentrated solutions, however, especially when the molecular weight of the solute is great, the two concentrations differ very considerably. For example, a solution containing 1 mol. of cane sugar in 1000 grams of water is 1 normal according to Raoult and 0·826 normal according to Arrhenius.

Direct measurements of the osmotic pressure of concentrated solutions by means of semipermeable membranes have been carried out with considerable accuracy for solutions of cane sugar and similar substances, and also for calcium ferrocyanide, by Lord Berkeley and Hartley, and by Morse, Frazer, and their collaborators.* As is shown in the tables, the measurements

* Landolt-Börnstein, 4th edition.

of the osmotic pressures deviate considerably from the laws of van't Hoff when expressed in terms of the volume concentration c. On the other hand, the proportionality between concentration and osmotic pressure remains fairly close when the concentration is expressed in terms of c'. The osmotic pressures at 0° and 10° are, however, considerably greater than we should expect from the gas laws. We shall endeavour later on to account for these deviations.

OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS.

c'.	c.*	π (atmospheres). 0°.	10°.	15°.	$\frac{\pi}{c}$ 0°.
0·10	0·098	2·44	2·44	2·48	24·9
0·20	0·192	4·80	4·82	4·91	25·0
0·30	0·282	7·16	7·19	7·33	25·4
0·40	0·369	9·40	9·57	9·78	25·45
0·50	0·452	11·85	12·00	12·19	26·2
0·60	0·532	14·25	14·54	14·86	26·8
0·70	0·610	16·8	17·09	17·39	27·5
0·80	0·686	19·3	19·73	20·09	28·1
0·90	0·757	22·1	22·22	22·94	29·2
1·00	0·826	24·8	24·97	25·42	30·0
		MOLECULAR OSMOTIC PRESSURE $\frac{\pi}{c'}$.			
0·1	—	24·4	24·4	24·8	—
0·2	—	24·0	24·1	24·55	—
0·3	—	23·9	24·0	24·4	—
0·4	—	23·5	23·9	24·45	—
0·5	—	23·7	24·0	24·6	—
0·6	—	23·6	24·2	24·8	—
0·7	—	24·0	24·4	24·8	—
0·8	—	24·1	24·8	25·0	—
0·9	—	—	24·7	25·6	—
1·0	—	—	25·0	25·4	—
		Mean 23·9	24·35	24·9	
		Calculated $\pi = \frac{RT}{c'} = 22·4$	23·2	23·6	

* The volume concentrations c refer to 0°; at higher temperatures the value of c' corresponding to the same value of c is slightly lower than at 0°, owing to the expansion of the solutions. The differences at 15° are, however, very small.

Trustworthy measurements of the osmotic pressure of non-aqueous solutions have not yet been carried out.* Numerous accurate researches on the boiling points and freezing points of non-aqueous solutions have, however, been carried out by Beckmann and his collaborators, and by a large number of other investigators. These show that the raising of the boiling point and the depression of the freezing point of solutions of non-electrolytes in nearly all solvents are proportional to the concentration by weight c' up to concentrations of $\frac{1}{2}$ normal.

The following tables were taken at random from the papers of Beckmann and Auwers.

RAISING OF THE BOILING POINT.

Taken from Beckmann (*Zeitschr. f. physikal. Chemie*, **18**, 473 (1895)).

Solvent: Ethyl bromide $T_0 = 273 + 37 = 310°$.
Solute: Camphor $C_{10}H_{16}O$, mol. wt. 152.

c'.	$T - T_0$.	$\frac{T - T_0}{c'}$.
0·143	0·455	3·18
0·338	1·130	3·34
0 552	1·840	3·34
0·717	2·390	3·33
0·893	2·990	3·35

Solvent: Methyl iodide, $T_0 = 273 + 41 = 314°$.
Solute: Diphenylamin $(C_6H_5)_2NH$, mol. wt. 169.

0·0875	0·360	4·12
0·189	0·780	4·13
0·270	1·110	4·12
0·337	1·370	4·07
0·418	1·690	4·04
0·526	2·110	4·01

* The measurements of Kahlenberg, Wilcox, and others (*Journ. Phys. Chem.* **10**, 141 (1906) and **14**, 576 (1910)) have clearly been carried out with membranes which were not completely semipermeable. As ebullioscopic and kryoscopic determinations with the solutions used by these authors have shown that van't Hoff's laws hold at least approximately for these solutions, it is clear that their pressure measurements must be subject to a systematic error. It is natural to look for this error in the properties of the membrane. See v. Antropoff, *Zeitschr. f. physikal. Chemie*, **76**, 721 (1911).

Solvent: Ethylene bromide, $T_0 = 273 + 129{\cdot}5 = 402{\cdot}5°$.
Solute: Benzil $(C_6H_5CO)_2$, mol. wt. 210.

c'.	$T - T_0$.	$\frac{T - T_0}{c'}$.
0·158	1·050	6·65
0·249	1·640	6·58
0·364	2·360	6·48
0·468	3·000	6·41
0·567	3 600	6·35
0·667	4·215	6·32

Solvent: Ethyl acetate, $T_0 = 273 + 75 = 348°$.
Solute: Naphthalene, $C_{10}H_8$, mol. wt. 128.

0·126	0·355	2·82
0·223	0·600	2·69
0·328	0·873	2·66
0·472	1·270	2·70
0·536	1·420	2·65
0·648	1·700	2·62
0·775	2·000	2·58
0·939	2·380	2·54

LOWERING OF THE FREEZING POINT.

From Auwers (*Zeitschr. f. physikal. Chemie*, **42**, 513 (1903)).

Solvent: *p*-Chlortoluol, $T_0 = 273 + 163°$.
Solute: Naphthalene, $C_{10}H_8$, mol. wt. 128.

0·075	0·417	5·57
0·146	0·817	5·59
0·274	1·517	5·54
0·361	2·000	5·54

Solvent: *p*-Toluidine, $T_0 = 273 + 198°$.
Solute: Naphthol, $C_8H_{10}O$, mol. wt. 122.

0·1155	0·640	5·54
0·255	1·370	5·36
0·402	2·117	5·25

These figures might lead us to assume that the osmotic pressures, and the colligative properties which are proportional to them in moderately concentrated solutions, were proportional to the concentration by weight and not to the concentration by volume. This again would appear to be a serious objection to

the kinetic theory of osmotic pressure, which must lead in the first instance to a relation between pressure and volume functions. This conclusion is, however, not necessarily binding. Equations (4*c*), p. 265, and (10), p. 270, apply only to infinitely dilute solutions, and to concentrated solutions for which the density is a linear function of the volume concentration. We know from experience that this latter condition is not fulfilled by the great majority of solutions. In most cases the density of the solution increases according to a higher power of the concentration than the first, and therefore, at least, in proportion to a quadratic function, such as

$$s = s_0 + \alpha c + \beta c^2.$$

Hence we have

$$s - c\frac{ds}{dc} < s_0.$$

and therefore

$$\pi = RTc < \frac{1000 s_0}{M} RT \ln \frac{p_0}{p} < \frac{1000 s_0}{M} L \frac{T - T_0}{T_0},$$

or

$$T - T_0 > \frac{RT \cdot T_0}{L'} c$$

(see equation 15, p. 272). The difference between the left and the right-hand side of the inequality is greater, the greater the concentration of the solution. As c' is generally greater than c, it is probable, or at least possible, in many solutions, that the osmotic pressure is in reality proportional to the concentration by volume. The raising of the boiling point and the lowering of the freezing point, however, are proportional to the concentration by weight. The substitution of T_0 for T on the right-hand side of the inequality corresponds for most solvents to an error of at most 1 per cent. for concentrations up to $1n$.

The deviations from the simple laws do not become considerable until the concentration exceeds $0{\cdot}5n$, except for solutes of high molecular weight (cane sugar, etc.), where the heat of dilution cannot as a rule be neglected.

Attempts to find a general relationship between the colligative properties of concentrated solutions and the concentration have as yet never been entirely satisfactory. This is mainly to be

attributed to the absence of the necessary experimental work for 0·5–2 normal solutions of non-electrolytes, that is, of systematic determinations of all the quantities which appear in the equations (namely, concentration by weight and by volume, heat of dilution, etc.). The theoretical interpretation of the data for solutions of electrolytes must be postponed until the behaviour of non-electrolytes has been explained. The dissociation of electrolytes introduces a new complication which cannot be treated with success until the osmotic pressure laws for concentrated solutions have been elucidated.

Two distinct methods of attack have been employed in the attempt to obtain an equation of state for concentrated solutions. Some investigators have tried to account for the deviations from van't Hoff's laws of osmotic pressure in concentrated solutions by applying van der Waals' reasoning to the theory of solution. It follows from the method by which the simple laws were deduced, that they can only be valid when the volume of the solute molecules and the forces acting between them are negligible. Indeed, the kinetic molecular conception of solutions demands the application of corrections to the simple laws when these conditions are not fulfilled, so that the deviations in concentrated solutions must be regarded as a confirmation and not as a contradiction of van't Hoff's theory of solution. On the other hand, some authors are of opinion that the relation between the colligative properties and the molecular concentration is the same for all solutions whether dilute or concentrated, and that the experimental deviations are only apparent exceptions, which can be explained by an alteration in the molecular concentration, that is to say, by association, dissociation, or formation of compounds between the solute and the solvent. Raoult's law for the lowering of the vapour pressure is usually taken by the exponents of this theory as the fundamental law of solutions, viz. (see p. 251)

$$\frac{p_0-p}{p_0}=\frac{c}{c_0+c} \quad \text{or} \quad \frac{p}{p_0}=\frac{c_0}{c_0+c}.$$

The ratios $\frac{c}{c_0+c}$ and $\frac{c_0}{c_0+c}$ are termed the mol fractions of solute and solvent respectively (see p. 233).

If the lowering of the vapour pressure and the quantities thermodynamically related to it, namely, the lowering of the freezing point, the raising of the boiling point, and the osmotic pressure, are found to be too large, this is explained by a diminution in the denominator, which in turn is attributed to the formation of compounds between solute and solvent, and a consequent decrease in the total number of molecules in the solution. On the other hand, if the lowering of the vapour pressure is too small, this is attributed to an increase in the number of molecules in the numerator, *i.e.* to a dissociation of previously associated molecules of the solvent. This point of view has undoubtedly proved of value in explaining the anomalous behaviour of solutions of electrolytes, and might at first sight seem applicable to concentrated solutions also.

In the following we shall deduce some of the formulae for the osmotic pressure, and for the changes in the vapour pressure, boiling point, and freezing point of solutions, which can be derived from these two essentially distinct theories of solution.

The kinetic theory of concentrated solutions. In applying van der Waals' equation

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

to solutions, we must remember that the added terms must account for the forces of attraction, and for the volume of both solute and solvent molecules. Bredig * was first in pointing out, however, that the force of attraction which the solute molecules exert on one another, and which tend to counteract the dilution (and hence the osmotic pressure), are compensated or perhaps exceeded by the attraction between solute and solvent which favours the process of dilution, and therefore increases the osmotic pressure. It is therefore probable that the correction for the molecular attraction is small enough to be neglected in moderately concentrated solutions. According to Nernst,† it is necessary to take into account the volume of the solute molecules alone, while the correction for the volume of the solvent molecules can be disregarded. Hence, in moderately

* *Zeitschr. f. physikal. Chemie*, **4**, 447 (1889).

† *Lehrbuch*, 1st ed. p. 193.

concentrated solutions, the osmotic pressure is represented by the equation

$$\pi(v-b)=RT,$$

in which b is four times the actual volume of the solute molecules (see p, 63), and $v=\frac{1}{c}$ is the volume of the solution which contains 1 mol. of the solute. From the measurements of Morse * and his collaborators on the osmotic pressure of cane sugar, Sackur † obtained values which are in excellent agreement with this equation.

The following table contains the experimental values of πv obtained by Morse for 0°, 10°, and 22°, and also the values of πv calculated from the equation

$$\pi v=RT+b\pi.$$

(The slight thermal expansion of the solution is neglected.)

$c=\frac{1}{v}$	0°.		10°.		22°.	
	$\pi v_{\text{found.}}$	πv_{calc}	πv_{found}	πv_{calc}	$\pi v_{\text{found.}}$	πv_{calc}
0·098	23·1	22·9	24·9	—	24·3	24·7
0·192	23·4	23·6	25·0	—	24·65	25·15
0·282	24·65	24·55	25·5	25·2	25·6	25·65
0·369	25·45	25·3	25·8	25·8	26·0	26·1
0·452	26·0	25·55	26·5	26·5	26·7	26·6
0·532	27·0	26·9	27·2	27·2	27·1	27·1
0·610	27·8	27·7	28·0	27·9	27·8	27·6
0·686	28·6	28·5	—	—	28·4	28·1
0·787	29·4	29·35	29·3	29·3	28·85	28·6
0·826	30·75	30·3	30·2	30·1	29·6	29·1
		$=22·4+0·31\pi$		$=23·2+0·275\pi$		$=24·2+0·20\pi$

The constant b decreases as the temperature rises, which may be explained by a decrease in the hydration.

Assuming the equation of state to be

$$\pi=\frac{RT}{v-b}=\frac{RTc}{1-bc},$$

* See p. 284.

† *Zeitschr. f. physikal. Chemie*, **70**, 477 (1910).

we obtain for the vapour pressure p, the boiling point, and the freezing point T, the following equations :

1. From $\pi = 1000 s_0 \cdot \frac{RT}{M} \cdot ln \frac{p_0}{p}$ (see p. 265),

we have $$ln \frac{p_0}{p} = \frac{M}{1000 s_0} \cdot \frac{c}{1 - bc}.$$

2. From $$\pi = \pm 1000 s_0 \cdot \frac{L}{M \cdot T}(T - T_0),$$

we have $$\frac{T - T_0}{T} = \pm \frac{MRT_0}{L \cdot 1000 s_0} \cdot \frac{c}{1 - bc}$$

(The positive sign refers to the freezing point, the negative sign to the boiling point.)

These equations differ from those for dilute solutions by the term $(1 - bc)$ in the denominator. The change in the vapour pressure, and in the boiling point and freezing point, is therefore relatively greater in concentrated than in dilute solutions. This result is confirmed qualitatively by experiment in almost every case, as a review of the literature of the subject will show (see in particular the researches of Abegg, Auwers, and others). It is clear from the primitive nature of the underlying assumptions that the above equations can only be accurate for a limited range of concentration.

A quantitative test of these relationships is not yet possible, as the heats of dilution of solutions of non-electrolytes have not been determined, and the available data on the vapour pressures of moderately concentrated solutions are too inaccurate.

For the partition law in concentrated solutions, it follows from

$$v_a d\pi_a = v_b d\pi_b$$

that $$\frac{dv_a}{v_a - b_a} = \frac{dv_b}{v_b - b_b},$$

and hence $$ln \frac{v_{a_2} - b_a}{v_{a_1} - b_a} = ln \frac{v_{b_2} - b_b}{v_{b_1} - b_b},$$

or $$\frac{v_a - b_a}{v_b - b_b} = k,$$

and from this $$v_a = kv_b + b_a - kb_b = kv_b + K.$$

Putting $v_a = \frac{1}{c_a}$ and $v_b = \frac{1}{c_b}$, we have

$$c_b = \frac{kc_a}{1 - Kc_a}.$$

Even up to very considerable concentrations this equation is in excellent agreement with the experiments of Jakowkin on the partition of iodine and bromine between various solvents.

Henry's law, or rather the deviations from it, may be used like the partition law to test the equation of state for concentrated solutions. We shall show that the osmotic pressure of a saturated solution of any gas may be calculated from the solubility of the gas and its variation with the pressure.

In the deduction of the partition law (p. 275) we showed by means of a reversible isothermal cycle that the osmotic pressures and the specific volumes of the solute in the two solvents A and B are related to one another by the equation

$$v_a \, d\pi_a = v_b \, d\pi_b.$$

This equation is a direct consequence of the laws of thermodynamics, and involves no assumptions as to the nature of solute and solvent.

If the solute be a gas and the solvent B be taken to be the vapour of A (or a vacuum if A is non-volatile), we obtain by an exactly similar line of reasoning the equation

$$\phi \, d\pi = v \, dp,$$

where $\phi = \frac{1}{c}$ is the specific volume of the gas in the solvent (A), π its osmotic pressure, and v and p are the specific volume and the partial pressure of the gas (solute) in the gaseous phase. Integrating this equation, we obtain for the osmotic pressure

$$\pi = \int_0^p \frac{v}{\phi} dp.$$

$\frac{v}{\phi}$ is the ratio of the molecular volumes of the gas in the gaseous and in the dissolved states. (This quantity was called the coefficient of absorption by Ostwald. Formerly Bunsen's definition of the coefficient of absorption was in common use,

viz. the volume of the gas which is absorbed by 1 c.c. of the solvent.) If $\frac{v}{\phi}$ is known as a function of the pressure, π can be calculated for all pressures.

If the gas laws are valid for the gaseous phase, and if Henry's law $\phi = \frac{1}{c} = \frac{1}{\alpha p}$ holds for the solubility, we have

$$\pi = \int_0^p \frac{RT}{p} \cdot \alpha p \cdot dp = \alpha RTp = RTc,$$

that is to say, the osmotic pressure obeys van't Hoff's law. On the other hand, if the solubility increases more rapidly with the pressure than would follow from Henry's law, we may write as a first approximation

$$c = \alpha p + \beta p^2,$$

and if the gas laws hold for the gaseous phase

$$\frac{v}{\phi} = RT(\alpha + \beta p),$$

and therefore $$\pi = \int_0^p RT(\alpha + \beta p)dp = RT(\alpha p + \tfrac{1}{2}\beta p^2).$$

Thus if α and β are known from solubility determinations, the osmotic pressure can be calculated for all concentrations from the solubility of the gas. The osmotic pressure of concentrated solutions of carbon dioxide in various organic solvents at low temperatures has recently been determined by O. Stern.* With the aid of the above formulae he found, in agreement with the kinetic theory, that the deviations from van't Hoff's laws are very slight even for concentrations of several times normal.

The chemical theory of concentrated solutions. This theory, which has been discussed already on p. 289, states that Raoult's law is always valid, and that apparent deviations are due to a change in the number of molecules in the solution.

Since $c_0 = \frac{1000s - Mc}{M_0}$ (M_0 is the molecular weight of the solvent), it follows from equation (a), p. 283, combined with

$$\frac{p_0 - p}{p_0} = \frac{c}{c_0 + c} \quad \text{or} \quad \frac{p_0}{p} = \frac{c_0 + c}{c_0},$$

* *Dissertation*, Breslau, 1912; *Zeit. f. physikal. Chemie*, **81**, 441 (1912).

that $$\frac{c}{c_0}=\frac{M_0c'}{1000} \quad \text{and} \quad \frac{c_0+c}{c_0}=1+\frac{M_0c'}{1000},$$

and hence that

$$\pi=1000s_0\frac{RT}{M_0}ln\frac{p_0}{p}=1000s_0\frac{RT}{M_0}ln\left(1+\frac{M_0c'}{1000}\right).$$

For small values of c' this equation becomes identical with

$$\pi=RTc,$$

but for larger values of c' the osmotic pressure deviates considerably from the laws of van't Hoff.

The boiling point and the freezing point of the solution are given by

$$\frac{T-T_0}{T}=\pm\pi\cdot\frac{M_0}{1000s_0}\cdot\frac{T_0}{L}=\pm\frac{RT_0}{L}\cdot ln\left(1+\frac{M_0c'}{1000}\right),$$

where the positive sign refers to the freezing point and the negative to the boiling point.

These equations apply only when there is no change in the number of the molecules during solution, as otherwise equation (a) is no longer accurate.

In dilute solutions

$$ln\left(1+\frac{M_0c'}{1000}\right)=\frac{M_0c'}{1000},$$

and in concentrated solutions

$$ln\left(1+\frac{M_0c'}{1000}\right)<\frac{M_0c'}{1000}.$$

The change in the boiling and freezing points should therefore be smaller than the values calculated from the simple laws of van't Hoff.

Experiment has shown that the reverse is true in the great majority of cases. This can only be made to agree with the chemical theory by assuming a diminution in the number of molecules, by the formation of compounds between the solvent and the solute (hydrate or solvate theory).

Thus, if the fraction x of the c' solute molecules, *i.e.* $c'x$ molecules, each combine with n molecules of the solvent to form

$c'x$ "solvate" molecules, then the total number of molecules in the solution is

$$g = c'(1-x) + c'x + \frac{1000}{M_0} - nxc'.$$

Hence

$$\frac{p_0 - p}{p_0} = \frac{c'}{\frac{1000}{M_0} + c'(1-nx)}$$

and

$$\frac{p_0}{p} = \frac{1 + \frac{M_0 c'(1-nx)}{1000}}{1 - \frac{M_0 c' nx}{1000}},$$

and correspondingly for the changes in the boiling and freezing points

$$\frac{T - T_0}{T} = \pm \frac{RT_0}{L} \cdot ln \left[\frac{1 + \frac{M_0 c'(1-nx)}{1000}}{1 - \frac{M_0 c' nx}{1000}} \right].$$

The expression in the square brackets can exceed $1 + \frac{M_0 c'}{1000}$ by an indefinite amount according to the values of n and x. Besides quantities which can be determined by experiment it involves, however, two further unknown quantities, namely x and n, which cannot be calculated without further assumptions.

Thus Jones,* W. Biltz,† and others have attempted to calculate the number of water molecules combined with the solute in aqueous solutions by assuming that $x = 1$, or, in other words, that the hydration of the solute is complete. These calculations lead, however, to somewhat improbable values for the number of combined water molecules n. On the other hand, assuming $n = 1$, Dolezalek has calculated the values of x for mixtures of organic liquids from the vapour pressure measurements of Zawidzki, and has succeeded in showing that the law of mass action holds for solvation as it does for other reactions.‡

* Summary, *Zeitschr. f. physikal. Chemie*, **74**, 325 (1910).

† *Zeitschr. f. physikal. Chemie*, **40**, 185 (1903).

‡ *Zeitschr. f. physikal. Chemie*, **64**, 727 (1908); **71**, 191 (1910).

If we extend the line of reasoning followed by these authors to account for the deviations from the laws of perfect gases, we should be led to conclude that these are also exclusively due to associations or dissociations.

This course has recently been taken by Drucker,* and it is not improbable that satisfactory figures may be calculated in this way. In accepting such a theory, however, we should be forced to give up entirely the great advance brought about by the theory of van der Waals.

It seems improbable therefore that the problem of concentrated solutions can be solved in this way.

* *Zeitschr. f. physikal. Chemie*, **68**, 616 (1909).

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CHAPTER IX.

THE LAWS OF CHEMICAL EQUILIBRIUM.

1. The law of mass action.

In Chapters VI. and VII. the various transformations of a single substance from one modification, or state of matter, to another were treated by the methods of thermodynamics. In the following we shall deal with transformations which are specifically chemical in character. Here, again, the laws of the equilibria can be derived from the laws of thermodynamics. The time which the transformation takes to come to completion (velocity of the reaction) cannot, however, be deduced in this way.

The simplest case, to which, as we shall see later, all the others can be reduced, is that of a chemical reaction which involves no change in phase, so that the reacting substances and the products of reaction are all parts of a common phase. This is the case when the substances concerned in the reaction are either all gases or all components of a homogeneous liquid solution. The solvent may be an inert substance taking no part in the reaction.*

The subsequent discussion is based on the theorem that all reactions in a homogeneous system come to a stop when a certain definite chemical equilibrium has been established between the substances which take part in the reaction. In other words, that such reactions never proceed so far that the substances entering into the reaction have disappeared entirely. All the

* It is no doubt possible in theory for a reaction to take place in a solid solution, but in practice this possibility is hardly worth considering.

elements or compounds which appear in the chemical equation by which the reaction is defined are present in finite, although often exceedingly small amounts at the conclusion of the reaction. This theorem has not yet proved susceptible of strict thermodynamical proof, nor is it possible to prove by experiment a law of such generality, applying as it does to all reactions in homogeneous systems. The principle of the continuity of all processes in nature, and also some thermodynamical evidence which we shall discuss later, justify us, however, in assuming its validity.

The first exact experimental proof of the existence of a chemical equilibrium in a homogeneous system is due to Berthelot and Péan de St. Giles. These investigators showed that the formation of an ester from an alcohol and an acid never goes to completion, but comes to a stop before the whole of the reacting substances have been transformed. In the same way the hydrolysis of esters into alcohol and acid ceases when equilibrium has been reached. Later, Deville and others noticed that many gaseous compounds, such as carbon dioxide and hydrogen chloride, which are apparently formed without residue from their components, can be split up into these components at high temperatures, as, for example,

$$2CO_2 = 2CO + O_2 \quad \text{and} \quad 2HCl = H_2 + Cl_2.$$

Reactions of this kind, which can go in one direction under certain conditions and in the opposite direction when the conditions are altered, are called reversible reactions. In writing the equation of a reversible reaction it is customary to use van't Hoff's symbol $\rightleftarrows$ instead of the sign of equality $=$. Thus, for the formation and decomposition of hydrogen chloride, we should write

$$H_2 + Cl_2 \rightleftarrows 2HCl.$$

The evidence which has been collected in the last two decades shows that all gaseous reactions, and also many reactions in solution, are reversible in this sense under the requisite conditions (thus the gas reactions above are reversed at high temperatures). By the principle of continuity we are then led to conclude that they are reversible under all conditions, and that the difficulty or impossibility under certain circumstances of

demonstrating their reversibility by analysis is due to the smallness of the equilibrium concentrations of some of the substances which take part in the reaction. Thus, all transformations in homogeneous systems may be regarded as reversible, and the classification into reversible and irreversible reactions is really superfluous. To avoid confusion with the reversible and irreversible processes of thermodynamics, it is better to give up the classification into reversible and irreversible chemical reactions, and use these words only in their thermodynamical sense.

By purely thermodynamical methods we can now deduce the following theorem: For every chemical reaction in a homogeneous system under constant external conditions (*e.g.* under constant temperature and pressure, or constant temperature and volume) there is a certain function of the concentrations of the components (no matter how these are expressed) which has a definite constant value when equilibrium is established. We may therefore write

$$F(c_1 c_2 \dots c_n) = K, \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

where c_1, c_2, ... c_n are the particular values of the concentrations of the n substances formed or destroyed in the reaction, at which the substances remain in presence of one another without reacting, and are therefore in equilibrium. K depends only on the variables of state (temperature and pressure or volume) and on the chemical nature of all the substances concerned (for solutions also on the nature of the solvents).

This equation may be interpreted as follows: If the concentration of any substance taking part in an equilibrium is altered while temperature and pressure, or temperature and volume, are kept constant, chemical action must proceed until the concentrations of all the components have assumed such values that equation (1) is again satisfied. To prove this we shall make use of the theorem that the change in entropy produced by an isothermal process in a system at equilibrium is $\frac{Q}{T}$ if the system remains at equilibrium throughout the process (see Chapter V. p. 142), or, in other words, if the process is reversible.

Consider a system at the uniform temperature T, made up of $n+1$ compartments, where n is the number of substances taking part in the chemical equilibrium. Let the first compartment contain an indefinite amount of the equilibrium mixture of the n substances, and let the n other compartments contain indefinite amounts of the pure reacting substances, each at the concentration (and therefore at the partial or osmotic pressure) which it has in the equilibrium compartment. Let us now transfer one equivalent of each of the r products of reaction by means of semipermeable membranes (or by any other reversible method) from the equilibrium compartment to the r compartments in which they are already present in the pure state. At the same time, let us replenish the equilibrium compartment with one equivalent from each of the other $n-r$ compartments containing the pure substances which disappear in the reaction. We can imagine these two processes to be carried out simultaneously in such a manner that the state of the equilibrium compartment and the concentrations (or pressures) of the n pure substances remain the same throughout. The entropy of the equilibrium compartment will then remain unaltered throughout the process. The change in the total entropy of the system is therefore $S_1 \pm S_2 \pm \ldots \pm S_n$, where S_1, S_2, $\ldots$ S_n are the entropies of unit mass (in equivalents) of the pure reacting substances. The positive signs correspond to the substances which appear, and the negative to those which disappear in the reaction. Hence, if the heat of reaction per equivalent at constant pressure be Q_p, we have the equation

$$S_1 \pm S_2 \pm \ldots \pm S_n = -\frac{Q_p}{T}.^* \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

This equation is the analytical expression of the second law of thermodynamics applied to chemical reactions. Equation (2) is equivalent to the general equation (1) as the quantities S_1, S_2, $\ldots$ S_n, and also $\frac{Q}{T}$ are definite functions of the concentrations c, the variables of state, and the chemical properties of the reacting substances.

* The negative sign appears because the change in entropy is equal to the heat *absorbed* divided by the temperature, while the heat of reaction is defined as the heat *evolved* in the reaction.

The analytical form of the function F cannot be derived by purely thermodynamical methods. For this purpose it is necessary to know the equation of state for each reacting substance. When the equations of state are given the entropy can be expressed as a function of the concentrations and the pressure and temperature.

The calculation is simple when all the reacting substances are perfect gases. In this case equation (1) transforms into the familiar "law of mass action."

For a perfect gas whose equation of state is $pv = RT$, and whose molecular heat c_v is independent of the temperature, the entropy S per mol. of the gas is given by

$$S = c_v \ln T + R \ln v + S' = c_v \ln T - R \ln c + S'. \quad \ldots\ldots\ldots(3)$$

Substituting this value of S in (2), we obtain the law of mass action and at the same time the integrated form of van't Hoff's equation for the heat of reaction (*Reaktionsisochore*). To illustrate the method, let us carry out the calculation for the formation of sulphur trioxide from sulphur dioxide and oxygen according to the equation $2SO_2 + O_2 = 2SO_3$.

For an isothermal and isopiestic change in the system at equilibrium, we have (as above) the equation

$$2S_{SO_3} - 2S_{SO_2} - 2S_{O_2} = -\frac{2Q_p}{T}. \quad \ldots\ldots\ldots(2a)$$

Q_p is the heat of formation of 1 mol. of SO_3 at constant pressure and at the temperature T. Substituting in (2a) the values of S_{SO_3}, S_{SO_2} and S_{O_2} given by equation (3), we obtain

$$(2c_{v_{SO_3}} - 2c_{v_{SO_2}} - c_{v_{O_2}}) \ln T - R \ln \frac{c^2_{SO_3}}{c^2_{SO_2} c_{O_2}} + 2S'_{SO_3} - 2S'_{SO_2} - 2S_{O_2} = -\frac{2Q_p}{T},$$

or, using the sign of summation for the specific heats and the entropy constants,

$$\ln \frac{c^2_{SO_3}}{c^2_{SO_2} c_{O_2}} = \frac{2Q_p}{RT} + \frac{\Sigma c_v}{R} \ln T + \frac{\Sigma S'}{R}. \quad \ldots\ldots\ldots(4)$$

We have assumed that all the gases taking part in the reaction are perfect, and hence that their total energies are independent of the pressure. The right-hand side of equation (4) is then independent of the concentrations, and depends only on the temperature and on the chemical nature of the reacting substances. We may therefore write (4) in the form

$$ln \frac{c_{SO_3}^2}{c_{SO_2}^2 c_{O_2}} = ln\, K \quad \text{or} \quad \frac{c_{SO_3}^2}{c_{SO_2}^2 c_{O_2}} = K.$$

For a reaction according to the general equation

$$\nu_a A + \nu_b B + \ldots = \nu_m M + \nu_n N + \ldots,$$

we obtain in a similar manner the equation

$$ln \frac{c_M^{\nu_m} \times c_N^{\nu_n} \times \ldots}{c_A^{\nu_a} \times c_B^{\nu_b} \times \ldots} = \frac{Q_p}{RT} + \frac{\Sigma c_v}{R} ln\, T + \frac{\Sigma S'}{R} = ln\, K. \quad \ldots\ldots(4a)$$

This is the general form of the law of mass action, first discovered empirically by Guldberg and Waage. A thermodynamic proof of this law by means of a reversible cycle was given later by van't Hoff. An isothermal and isopiestic change in the volume of a mixture of gases in chemical equilibrium thus leaves the value of the term on the left-hand side of equation (4*a*) unaltered. As a change in volume (without chemical action) would affect all the concentrations in the same way, it follows that an isothermal alteration in volume must be accompanied by a chemical displacement of the equilibrium, unless the sum of the indices of the concentrations is the same in numerator and denominator; in other words, unless the reaction proceeds without change in volume. In all other cases the equilibrium is displaced by a compression in the direction which involves a diminution in the number of molecules (principle of Le Chatelier and Braun).

The law of mass action remains valid when partial pressures are substituted for concentrations. By the gas laws we have $p_A = RTc_A$, etc., and hence

$$ln\, c_A = ln\, p_A - ln\, RT.$$

Writing $\nu = \nu_m + \nu_n + \ldots - \nu_a - \nu_b - \ldots$ for the diminution (or

increase) in the number of molecules caused by the reaction, we have

$$ln \frac{c_M^{\nu_m} c_N^{\nu_n} \cdots}{c_A^{\nu_a} c_B^{\nu_b} \cdots} = ln \frac{p_M^{\nu_m} p_N^{\nu_n} \cdots}{p_A^{\nu_a} p_B^{\nu_b} \cdots} - \nu \, ln \, RT,$$

and hence

$$ln \frac{p_M^{\nu_m} p_N^{\nu_n} \cdots}{p_A^{\nu_a} p_B^{\nu_b} \cdots} = ln \, K + \nu \, ln \, RT = ln \, K'. \quad \ldots\ldots\ldots\ldots (4b)$$

The equilibrium constants K and K' are equal to one another when the reaction involves no increase in the number of molecules, *i.e.* in the total volume. Otherwise the difference between them is $(RT)^{\nu}$.

An excellent confirmation of the law of mass action for the sulphur trioxide equilibrium is due to Bodenstein and Pohl.* Their experimental determinations at 1000° abs. = 727° C. are given (in atmospheres) in the following table :

p_{SO_3}.	p_{SO_2}.	p_{O_2}.	K'.
0·325	0·273	0·402	3·56
0·338	0·309	0·353	3·38
0·364	0·456	0·180	3·54
0·365	0·470	0·167	3·51
0·355	0·481	0·164	3·32
0·334	0·564	0·102	3·48
0·333	0·566	0·101	3·47
		Mean	3·48

In the first experiment equilibrium was reached by allowing SO_3 to dissociate, in all the others by the combination of SO_2 and O_2.

In the deduction of the law of mass action, we assumed that the reacting gases obeyed the gas equation $pv = RT$, and that their specific heats were independent of the temperature. We shall show later on that the first assumption alone would have been sufficient, so that the law of mass action is also valid for gases whose specific heats vary considerably with the temperature. In the meantime, however, we shall continue to assume, as a first approximation, that both conditions are fulfilled.

* *Zeitschr. f. Elektrochemie*, **11**, 373 (1905)

The variation of the equilibrium constant K with the temperature is given by equation (4*a*), namely

$$ln\,K = \frac{Q_p}{RT} + \frac{\Sigma c_v}{R} ln\,T + \frac{\Sigma S'}{R}.$$

The direction in which K changes with the temperature becomes apparent on differentiation. Thus we obtain

$$\frac{d\,ln\,K}{dT} = -\frac{Q_p}{RT^2} + \frac{1}{RT}\frac{dQ_p}{dT} + \frac{\Sigma c_v}{RT}.$$

On p. 127 we showed that the differential coefficient of Q_p with respect to the temperature is equal to the change in the specific heats, so that

$$\frac{dQ_p}{dT} = -\Sigma c_p = -\Sigma(c_v + R),$$

and hence

$$\frac{d\,ln\,K}{dT} = \frac{-Q_p}{RT^2} - \frac{\Sigma R}{RT} = -\frac{Q_p + \Sigma RT}{RT^2} = -\frac{Q}{RT^2}, \quad \ldots\ldots\ldots(5)$$

where Q is the heat of reaction at constant volume.

This is the well-known equation for the "reaction isochore" discovered by van't Hoff. The equation tells us qualitatively that the equilibrium constant increases with the temperature for endothermic reactions ($Q<0$), and diminishes with the temperature for exothermic reactions ($Q>0$). In other words (since the products of the reaction are in the numerator of the constant), an increase in the temperature favours the production of the substances which are formed with absorption of heat. We can test the equation quantitatively if we assume the heat of reaction to be constant and integrate for a small range of temperature. This assumption is justified by experience, as the quantity $\frac{dQ}{dT} = -\Sigma c_v$ is always found to be small.

We have, therefore,

$$\int_{T_1}^{T_2} d\,ln\,K = -\int_{T_1}^{T_2} \frac{Q}{RT^2}\,dT,$$

and hence

$$ln\frac{K_2}{K_1} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{Q(T_1 - T_2)}{RT_1T_2}. \quad \ldots\ldots\ldots(6)$$

The equilibrium constant K_2 at the temperature T_2 can thus be calculated from the heat of reaction Q (at constant volume), and the equilibrium constant K_1 at the temperature T_1.

Equation (6) can be tested experimentally by determining K_1 and K_2 at two neighbouring temperatures T_1 and T_2, and comparing the value of Q calculated from the equation with calorimetric determinations of the heat of reaction. If the equilibrium constant be expressed in terms of the partial pressures (K'), Q must be replaced by the heat of reaction Q_p at constant pressure, which differs from Q by the work done in the reaction, viz. νRT. Thus we have

$$ln\, K' = ln\, K + \nu\, ln\, RT,$$

$$\frac{d\, ln\, K'}{dT} = \frac{d\, ln\, K}{dT} + \frac{\nu}{T} = \frac{-Q}{RT^2} + \frac{\nu}{T} = -\frac{Q - \nu RT}{RT^2} = \frac{-Q_p}{RT^2}, \quad \ldots(5a)$$

where $Q_p = Q - \nu RT$.

The experimental confirmation of (6) is well illustrated by the work of Bodenstein and Pohl on the formation of sulphur trioxide.

T.	$ln\, K'_{exp.}$	$ln \frac{K_2'}{K_1'}$.	$T_2 - T_1$.	$Q_{calc.}$	Q determined at room temperature.
801	6·67	—	—	—	—
900	3·66	3·01	99	43800	—
1000	1·25	2·41	100	43300	45200
1105	−0·78	2·03	105	42700	—

The calculated values of Q agree excellently with the experimental determinations at the ordinary temperature if we allow for the fact that the heat of reaction diminishes as the temperature is raised.

Before testing the correctness of equation (4), let us consider what form the law of mass action will assume for gases which conform to the equation $pv = RT$ with sufficient accuracy, but whose specific heat varies with the temperature. Equation (3) can then no longer be applied, but must be replaced by

$$S = \int \frac{c_v}{T} dT + R\, ln\, v + S' = \int \frac{c_v}{T} dT - R\, ln\, c + S', \quad \ldots\ldots(7)$$

where c_v is a function of T (see Chapter V. p. 142). The integration can only be carried out when the form of this function is known.

From (7) and (2a), we have

$$ln \frac{c_M^{\nu_m} c_N^{\nu_n} \cdots}{c_A^{\nu_a} c_B^{\nu_b} \cdots} = \frac{Q_p}{RT} + \frac{1}{R}\int \frac{\Sigma c_v}{T} dT + \frac{\Sigma S'}{R}.$$

The right-hand side of the equation is again a function of T alone, and is constant when the temperature is constant. We may still write it therefore in the form $ln\ K$ (where K is independent of the concentrations), so that the law of mass action still holds (see p. 303).

Van't Hoff's equation is also valid in this case, for by differentiation we obtain

$$\frac{d\ ln\ K}{dT} = \frac{-Q_p}{RT^2} + \frac{1}{RT}\frac{dQ_p}{dT} + \frac{\Sigma c_v}{RT} = -\frac{Q}{RT^2},$$

since $$\frac{dQ_p}{dT} = -\Sigma(c_v + R)$$

as before. The equilibrium constant K, however, is now given as a function of the temperature by the equation

$$ln\ K = \frac{Q_p}{RT} + \frac{1}{R}\int \frac{\Sigma c_v}{T} dT + \frac{\Sigma S'}{R}. \quad \ldots\ldots\ldots\ldots\ldots(8)$$

Equations (4a) and (8) have only quite recently been subjected to the test of experiment, chiefly by Haber and Nernst. For historical reasons both Nernst and Haber make van't Hoff's equation their starting point.

Expanding c_v* in powers of T, viz.

$$c_v = c_{v_0} + \beta T + \gamma T^2 + \ldots,$$

and then integrating the equation

$$\frac{dQ}{dT} = -\Sigma c_v,$$

we obtain $$Q = -\int \Sigma(c_{v_0} + \beta T + \gamma T^2 + \ldots) dT + Q_0$$

$$= Q_0 - \Sigma c_{v_0} T - \frac{\Sigma\beta}{2} T^2 - \frac{\Sigma\gamma}{3} T^3 \ldots,$$

* c_v is the true specific heat.

and hence

$$ln\,K = \int \frac{-Q}{RT^2}\,dT + J$$

$$= \frac{Q_0}{RT} + \frac{\Sigma c_{v_0}}{R} ln\,T + \frac{\Sigma\beta}{2R}T + \frac{\Sigma\gamma}{6R}T^2 \ldots + J. \quad \ldots\ldots\ldots(9)$$

This equation (9) may, of course, be obtained from (8) directly by expanding Q and Σc_v in power series, viz.

$$Q_p + \nu RT = Q = Q_0 - \Sigma c_v\,T - \frac{\Sigma\beta}{2}T^2 - \frac{\Sigma\gamma}{3}T^3$$

and $$\Sigma c_v = \Sigma c_{v_0} + \Sigma\beta T + \Sigma\gamma T^2 + \ldots.$$

Equation (4a) is a special case of (9), in which $\beta = \gamma = \ldots = 0$, and hence $c_v = c_{v_0}$. Comparing (8) and (9), we see further that

$$J = \frac{\Sigma(S' - c_{v_0} - R)}{R} = \frac{\Sigma(S' - c_{p_0})}{R}, \quad \ldots\ldots\ldots\ldots(10)$$

where $c_{p_0} = c_{v_0} + R$ is the value of the specific heat at constant pressure, for $T = 0$, *i.e.* at the absolute zero. The indeterminate integration constant of van't Hoff's equation can therefore be expressed as a sum of constants which are characteristic of each reacting substance. Nernst derived this result in 1906 from his "heat theorem," which we shall discuss in full later on. Equation (10) is, however, independent of Nernst's "heat theorem." This is shown by the above purely thermodynamical proof. The older demonstrations of Planck * and Haber † lead to the same result, and differ only slightly in form from the above (see note to p. 143).

In terms of partial pressures equation (9) becomes

$$ln\,K' = \frac{Q_{p_0}}{RT} + \frac{\Sigma c_{p_0}}{R} ln\,T + \frac{\Sigma\beta}{2R}T + \frac{\Sigma\gamma}{6R}T^2 + \ldots$$

$$+ \Sigma\frac{(S' + R\,ln\,R - c_{p_0})}{R}. \ddagger \quad \ldots(9a)$$

* *Thermodynamik*, 1st edition, 1897, p. 205.

† *Thermodynamik technischer Gasreaktionen*, Munich, 1905, p. 38.

‡ We may note that $S' + R\,ln\,R$ is the constant S_p' in the equation

$$S = c_p\,ln\,T - R\,ln\,p + S_p',$$

which is equivalent to equation (3), p. 301, when p and T are taken as independent variables.

Knowing the values of the entropy constants S', and also the specific heats and their temperature coefficients (*i.e.* β, γ, ...) for all gases, we should be able to calculate the equilibrium constant K from the heat of the reaction for all gas reactions at all temperatures. The constants c_{v_0}, β, γ, ... can be determined for each gas by direct measurements of the specific heats at different temperatures. The two laws of thermodynamics alone, however, do not enable us to express the entropy constants S' in terms of experimental data. This has only recently been made possible by the discovery of Nernst's heat theorem (see Chapter XIV.).

As long as we are ignorant of the values of the entropy constants S', the calculation of the equilibrium constant K from thermal data can only be carried out by actually determining K at a chosen temperature T, and then calculating the integration constant J from equation (9). When this has been done, however, we are in a position to predict the position of the chemical equilibrium, and hence the reactivity of the gases for all other temperatures.

In the meantime this problem can only be solved to a certain degree of approximation. In the first place the constants c_{v_0}, β, γ, ... are not accurately known, as they can only be obtained by fitting a formula containing several constants to a limited number of experimental data. Besides this, the gas equation $pv = RT$ is not strictly accurate for real gases, especially for polyatomic gases such as H_2O, CO_2, SO_2, etc.

Haber and Nernst have nevertheless succeeded in obtaining equations of the form (9) which agree very well with the experimental determinations of K. The experimental methods of investigating gaseous equilibria are not within the scope of this book. A detailed discussion of them will be found in Nernst's text-book.

We shall now illustrate the application of equations (4*a*) and (9) by some numerical examples. The numerical values of the constants β, γ, etc., are generally small in practice, so that the corresponding terms in the equation are relatively inconsiderable, especially when the heat of reaction Q_p is great. In the following calculation we shall assume as a first approximation that the

specific heat is constant. We shall further make use of the assumption (supported by theory and experiment) that the specific heat of a gas is determined by the number of atoms in the molecule (see Chapter V. p. 163). Thus we shall take the molecular heat c_v to be 3 for all monatomic gases, 5 for all diatomic gases (O_2, N_2, CO, H_2, etc.), and 6 for all triatomic gases (H_2O, CO_2, etc.). Although these assumptions are certainly not strictly accurate, the errors introduced by them are apparently so slight as not to invalidate the theoretical formulae.

Making use of these assumptions, we have the equation (4*a*)

$$ln\, K = \frac{Q_p}{RT} + \frac{\Sigma c_v}{R} ln\, T + \frac{\Sigma S'}{R}.$$

Q_p is the heat of reaction (at constant pressure) at the temperature T, and can be calculated from the heat of reaction Q_{p_0} at the temperature T_0 (usually room temperature) by means of a linear formula $Q_p = Q_{p_0} - \Sigma c_p (T - T_0)$. Hence we obtain

$$\left.\begin{aligned} ln\, K &= \frac{Q_{p_0}}{RT} - \frac{\Sigma c_p}{R} \cdot \frac{T - T_0}{T} + \frac{\Sigma c_v}{R} ln\, T + \frac{\Sigma S'}{R} \\ &= \frac{Q_{p_0}}{RT} + \frac{\Sigma c_p}{R} \cdot \frac{T_0}{T} + \frac{\Sigma c_v}{R} ln\, T + \frac{\Sigma (S' - c_p)}{R}. \end{aligned}\right\} \quad \ldots\ldots\ldots(11)$$

As Σc_v and Σc_p are given by the above assumptions, it is possible to calculate K for all temperatures from two experimental determinations, viz. a determination of Q_{p_0} at the temperature T_0, and a determination of the equilibrium constant K at any chosen temperature. Introducing partial pressures in place of concentrations, we obtain (as on p. 303)

$$ln\, K' = ln\, K + \nu\, ln\, R + \nu\, ln\, T,$$

and hence, by (10) and (11),

$$ln\, K' = \frac{Q_{p_0}}{RT} + \frac{\Sigma c_p}{R} \frac{T_0}{T} + \frac{\Sigma c_v + \nu R}{R} ln\, T + \underbrace{J + \nu\, ln\, R}_{J'},$$

and since $$\Sigma c_v + \nu R = \Sigma (c_v + R) = \Sigma c_p,$$

$$ln\, K' = \frac{Q_{p_0}}{RT} + \frac{\Sigma c_p}{R} \frac{T_0}{T} + \frac{\Sigma c_p}{R} ln\, T + J'. \quad \ldots\ldots\ldots(11a)$$

Let us test the approximate equation (11*a*) by calculating with its aid the dissociation of water vapour. This is, perhaps, the best gas reaction for the purpose, as it has been carefully investigated in several different ways by Nernst and his pupils. (The degree of dissociation has been determined between 1300° and 2300° absolute.) Let x per cent. be the degree of dissociation of water vapour at a total pressure of 1 atmosphere. The equation for the dissociation is $2H_2O = 2H_2 + O_2$, and hence the partial pressure of hydrogen is $p_{H_2} = \frac{x}{100}$ and of oxygen $p_{O_2} = \frac{x}{200}$. Since x is a small quantity, the partial pressure of the undissociated water vapour is approximately $p_{H_2O} = 1$. Hence

$$K' = \frac{p^2_{H_2O}}{p^2_{H_2} p_{O_2}} = \frac{100^2 . 200}{x^3} = \frac{2 \times 10^6}{x^3}.$$

The constants of equation (11*a*) have the following values:

$$Q_{p_0} \text{ at } T_0 = 373° \text{ abs. is } 116000 \text{ cal.},$$

$$\Sigma c_p = 2c_{p_{H_2O}} - 2c_{p_{H_2}} - c_{p_{O_2}} = 2 \times 8 - 2 \times 7 - 7 = -5,$$

and $R = 2$.

Substituting the decadic logarithm for the natural logarithm, we have $\left(\text{putting } \frac{J'}{2{\cdot}3} = J''\right)$,

$$\log K' = \frac{116000}{2{\cdot}3 \times 2T} - \frac{2{\cdot}5 \times 373}{2{\cdot}3T} - 2{\cdot}5 \log T + J''.$$

The constant J'' may be calculated from the value of the degree of dissociation at 1500° abs. (determined by Nernst and von Wartenberg), which we may assume to be perfectly reliable. They found at this temperature $x = 2{\cdot}0 + 10^{-2}$, and hence $\log K' = 11{\cdot}4$, so that

$$J'' = 11{\cdot}4 - \frac{116000}{4{\cdot}6 \times 1500} + \frac{2{\cdot}5 \times 373}{2{\cdot}3 \times 1500} + 2{\cdot}5 \times 3{\cdot}18 = 2{\cdot}8.$$

The equation for $\log K'$ as a function of T thus finally assumes the form

$$\log K' = \frac{24800}{T} - 2{\cdot}5 \log T + 2{\cdot}8. \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

The following table contains the experimental values of x,* the values of the equilibrium constant $\log K'_{exp.}$ calculated

* Nernst, *Lehrbuch*, 6th edition, p. 680.

from these experimental data, the values of $\log K'_{\text{calc.}}$ derived from (12), and finally the values of x calculated from $\log K'_{\text{calc.}}$:

T.	$x_{\text{exp.}}$	$\log K'_{\text{exp}}$	$\log K'_{\text{calc}}$	$x_{\text{calc.}}$	$\log K'_{\text{calc}}$ N.
1300	$2{\cdot}7\times10^{-4}$	14·00	14·15	$2{\cdot}4\times10^{-4}$	13·97
1397	$7{\cdot}8\times10^{-3}$	12·13	12·73	$7{\cdot}2\times10^{-3}$	—
1480	$1{\cdot}9\times10^{-2}$	11·47	11·66	$1{\cdot}6\times10^{-2}$	11·26
1500 *	$2{\cdot}0\times10^{-2}$	11·41	11·41	$2{\cdot}0\times10^{-2}$	—
1561	$3{\cdot}4\times10^{-2}$	10·74	10·74	$3{\cdot}3\times10^{-2}$	—
1705	$1{\cdot}0\times10^{-1}$	9·28	9·28	$1{\cdot}0\times10^{-1}$	9·15
2155	1·2	6·09	5·97	1·3	6·09
2257	1·8	5·55	5·41	2·0	—
2300	2·6	5·06	5·13	2·5	5·33

The figures given in the last column will be discussed later on. The agreement between the experimental and calculated values is very good. This shows that the assumptions we have made with regard to the values of the specific heats enable us to predict the position of the equilibrium (from a single experimental determination) for a very considerable range of temperature.

The agreement between theory and experiment holds good for other gas reactions, and is not merely accidental. Another example is the dissociation of carbon dioxide according to the equation $2CO_2=2CO+O_2$. In the following table $x_{\text{exp.}}$ is the degree of dissociation (per cent.) of CO_2 at a total pressure of 1 atmosphere,† and $\log K'_{\text{exp.}}$ is the equilibrium constant calculated from $x_{\text{exp.}}$. The heat of reaction at the ordinary temperature (300° abs.) is 13600 cal., and $\Sigma c_p=2\times8-2\times7-7=-5$. The constant J'' is calculated from the value of $x_{\text{exp.}}$ at 1443°, viz. $x=2{\cdot}5\times10^{-2}$. Thus

$$J''=11{\cdot}11-\frac{136000-5\times300}{2{\cdot}3\times2\times1443}+2{\cdot}5\log1443=-1{\cdot}24.$$

The equation for $\log K'_{\text{calc.}}$ is therefore

$$\log K'_{\text{calc.}}=\frac{29250}{T}-2{\cdot}5\log T-1{\cdot}24, \quad \text{.....(13)}$$

* Used in the calculation of J'. † Taken from Abegg's *Handbuch*, 4, p. 183.

and for $x_{\text{calc.}}$, we have

$$K'_{\text{calc.}} = \frac{2 \times 10^6}{x^3_{\text{calc.}}}.$$

T.	x_{exp}	$\log K'_{\text{exp}}$	$\log K'_{\text{calc}}$	x_{calc}
1300	$4{\cdot}14 \times 10^{-3}$	13·45	13·48	$4{\cdot}08 \times 10^{-3}$
1395	$1{\cdot}42 \times 10^{-2}$	11·86	11·87	$1{\cdot}38 \times 10^{-2}$
1400	2×10^{-2}	11·4	11·75	$1{\cdot}51 \times 10^{-2}$
1443*	$2{\cdot}5 \times 10^{-2}$	11·11	11·11	$2{\cdot}5 \times 10^{-2}$
1478	$2{\cdot}9$–$3{\cdot}5 \times 10^{-2}$	10·91–10·67	10·64	$3{\cdot}55 \times 10^{-2}$
1498	$4{\cdot}71 \times 10^{-2}$	10·28	10·32	$4{\cdot}58 \times 10^{-2}$
1500	4×10^{-2}	10·49	10·31	$4{\cdot}58 \times 10^{-2}$
1565	$6{\cdot}4 \times 10^{-2}$	9·89	9·44	$9{\cdot}3 \times 10^{-2}$

The differences between $x_{\text{calc.}}$ and $x_{\text{exp.}}$ are generally within the experimental error. The only serious error is at 1565°, and is possibly due to a faulty observation.

As a third example of the utility of the approximate equation (11a), let us calculate the dissociation of iodine vapour ($I_2 = 2I$).† In this case the heat of reaction Q_p is unknown, but the observations are nevertheless in agreement with an equation of the form (11a). We have here

$$\Sigma c_p = c_{p_{I_2}} - 2c_{p_I} = 7 - 2 \times 5 = -3$$

and

$$\log K' = \frac{Q_{p_0} - 3T_0}{2{\cdot}3 \times 2 \times T} - 1{\cdot}5 \log T + J''.$$

For Q_{p_0} and J'' we have, by a simple calculation,

$$4{\cdot}6 \times T \log K' + 6{\cdot}9T \log T = Q_{p_0} - 3T_0 + 4{\cdot}6TJ''.$$

The left-hand side of this equation should therefore be a linear function of T.

T.	$\log K'$.	$Q_{p_0} - 3T_0 + 4{\cdot}6TJ''$ $= 4{\cdot}6T \log K' + 6{\cdot}9T \log T$.	$\log K'_{\text{calc}}$
1073	1·945	32000	1·93
1173	1·325	31950	1·31
1273	0·782	31830	0·77
1373	0·309	31700	0·30
1473	−0·091	31600	−0·10

* Taken from Abegg's *Handbuch*, 4, p. 183.

† Bodenstein and Starck, *Zeitschr. f. Electrochemie*, **16**, 961 (1910).

The figures in the third column are nearly constant. For an increase in temperature of 400° the decrease is only 400 cal. From this we calculate $J'' = -0{\cdot}22$ and $Q_{p_0} - 3T_0 = 33000$ cal. The heat of formation of the iodine molecule at room temperature (300° abs.) is therefore 33900 cal.

For the dissociation constant of iodine at any temperature, we have therefore

$$\log K' = \frac{33000}{4{\cdot}6T} - 1{\cdot}5 \log T - 0{\cdot}22$$

$$= \frac{7180}{T} - 1{\cdot}5 \log T - 0{\cdot}22. \quad \ldots\ldots\ldots\ldots (14)$$

The last column of the above table contains the values of $\log K'$ calculated by this formula. The agreement with the second column proves the utility of the equation.

The calculation of the equilibrium constant by equation (9) is usually a lengthy proceeding. For this purpose it is necessary to know the true specific heats, or the variation of the specific heats with the temperature. For the dissociation of water vapour, Nernst calculates from the mean specific heats of H_2O, H_2, and O_2 an equation which, after the necessary transformation for $K' = \frac{2 \times 10^6}{x^3}$, may be written in the form

$$\log K' = \frac{25030}{T} - 2{\cdot}38 \log T + 1{\cdot}38 \times 10^{-4} T + 0{\cdot}685 \times 10^{-7} T^2 + 1{\cdot}81.$$

The values calculated by this equation are given under the heading $\log K'_{\text{calc.}} N$ in the last column of the table on p. 311. We may say without exaggeration that the experimental figures agree quite as well with the approximate equation as with this more accurate equation. As far as the dissociation of water vapour is concerned, the correction for the variation of the specific heats would therefore appear to be superfluous. The same remark applies to the other reactions which we have just been considering.

The approximate formulae become very much simpler for gas reactions which are not accompanied by an increase in the number of molecules, such as the formation of nitric oxide,

$$N_2 + O_2 = 2NO.$$

Here $\Sigma c_p = 0$, so that the heat of reaction is independent of the temperature. Equation (4*a*) therefore simplifies to

$$\ln K = \frac{Q}{RT} + J, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

so that the logarithm of the equilibrium constant is a linear function of $\frac{1}{T}$. This equation represents the nitric oxide equilibrium very well. Taking the heat of formation of 2 mols. of NO to be -43200 and using decadic logarithms, Nernst found the value of J to be $+1{\cdot}09$.*

The simple approximate equation (15) is also in good agreement with the " water gas " equilibrium,

$$CO_2 + H_2 = CO + H_2O.$$

In this case, indeed, the integration constant can be derived from data which we have already calculated. The equilibrium constant K_3 of this reaction can be calculated from the dissociation constant of water K_1' and of carbon dioxide K_2'. Thus we have

$$K_3 = \frac{p_{CO} \cdot p_{H_2O}}{p_{CO_2} \cdot p_{H_2}} = \sqrt{\frac{p^2_{H_2O}}{p^2_{H_2} \cdot p_{O_2}} \cdot \frac{p^2_{CO} \cdot p_{O_2}}{p^2_{CO_2}}} = \sqrt{\frac{K_1'}{K_2'}}$$

or

$$\log K_3 = \tfrac{1}{2} \log K_1' - \tfrac{1}{2} \log K_2'.$$

Hence, by (12) and (13),

$$\log K_3 = -\frac{2200}{T} + 2{\cdot}0.$$

The following table gives the values of K_3 calculated by this equation and determined experimentally by O. Hahn † at various temperatures : †

$T_{abs.}$	$\log K_{3\,exp.}$	$\log K_{3\,calc.}$
959	$-0{\cdot}272$	$-0{\cdot}29$
1059	$-0{\cdot}075$	$-0{\cdot}08$
1159	$+0{\cdot}08$	$+0{\cdot}10$
1209	$0{\cdot}20$	$+0{\cdot}18$

* Nernst, *Thermodynamics and Chemistry*, New York, 1907, p. 36.

† Taken from Haber, *Thermodynamik techn. Gasreaktionen*, p. 172.

The agreement shows that the approximate equations (12) and (13) can be used for several hundred degrees below the temperatures at which they can be tested directly.

2. Chemical affinity.

The equilibrium constant and its variation with the temperature are of great importance in theoretical chemistry, as they give us a quantitative and relatively easily determined measure of the strength of the chemical forces, so-called "chemical affinity." It is clear from the following consideration that there must be at least a qualitative relationship between the equilibrium constant and the chemical forces. The stronger the forces causing the combination of two substances, the more completely will they combine with one another, and the more difficult will it be to split up the resulting compound. The affinity is therefore greater the more the equilibrium favours the formation of the compound, or, in other words, the greater the equilibrium constant. This idea was familiar long ago to Berthollet and others as a way of comparing the chemical affinity of similar substances.* It was not until 1883, however, by a happy definition of chemical affinity, that van't Hoff succeeded in showing its thermodynamical relationship to the equilibrium constant.

In physics it is customary to measure the force causing any process by comparison with an opposing force just sufficient to bring the process to a stop. If the opposing force be small, the driving force of the system will be able to overcome it and do work. The amount of work done will be greater the greater the opposing force, that is, the smaller the difference between it and the driving force exerted by the system when in equilibrium. The work done will be a maximum for any given system when the opposing force and the driving force are equal to one another or differ only by an infinitesimal amount. The velocity of the change is then infinitely small, as the process is practically stopped by the opposing force. Thus the work done in the evaporation of water is greater the greater the pressure

* For a discussion of the historical development and the present state of our knowledge of chemical affinity, see O. Sackur, *Die chemische Affinität und ihre Messung*. Sammlung Wissenschaft. Braunschweig, 1908.

which the piston driven by the steam has to overcome. The work done in the evaporation will be a maximum when the piston has to overcome a pressure which is exactly equal to the saturation pressure of the steam in the boiler.

The work w done by the evaporating steam is equal to the product of the force f exerted on the piston and the distance s which it traverses. The force f is equal to the pressure p (force per unit surface) multiplied by the area o of the piston, *i.e.* $w = fs = pos = pv$, where v is the increase in the internal volume of the cylinder during the evaporation. The work done is therefore proportional to the amount of water evaporated.

Similarly, the work done against an opposing force by a system undergoing a chemical change is proportional to the amount of substance transformed by the reaction. The maximum work done in the transformation of unit mass—one equivalent of each substance—can only be expressed in terms of the opposing force when the chemical driving force and the external opposing force are equal to one another. Van't Hoff took the work obtainable in the transformation of unit mass as a measure of the chemical affinity. This definition of the affinity as an amount of work done enables us to measure affinity in terms of mechanical, electrical, and thermal quantities.

It is remarkable that the "force of affinity" should be measured by an amount of work, and not directly by the opposing force necessary to keep the system in equilibrium. The experimental realisation of a reaction kept in equilibrium by an external force is, however, only possible in rare cases, whereas we shall show in the following that there are a number of ways of determining the maximum work which the reaction is capable of yielding.

The calculation of the affinity is simple when the reacting substances are gases. We shall again illustrate the derivation of the equations by an actual example. Let us calculate the affinity between sulphur dioxide and oxygen tending to cause the combination of these two gases to sulphur trioxide. It is sufficient for this purpose to calculate the work which 2 mols. of SO_2 and 1 mol. of O_2 would yield by combining at constant temperature in any reversible manner. We know from the

second law of thermodynamics that any reversible isothermal method of carrying out the reaction must yield the same maximum amount of work.

Let the temperature of both gases be T, and let the 2 mols. of SO_2 occupy the volume $2v_{SO_2}$, so that its concentration is $c_{SO_2}=\frac{1}{v_{SO_2}}$. Let the volume of the mol. of oxygen be v_{O_2} and its concentration $c_{O_2}=\frac{1}{v_{O_2}}$. At the conclusion of the reaction we shall have 2 mols. of SO_3 at the same temperature T. Let the volume of the SO_3 be v_{SO_3} and its concentration $c_{SO_3}=\frac{1}{v_{SO_3}}$.

Now let the reaction proceed in the first instance so that 2 mols. of SO_3 of concentration c'_{SO_3} are produced. This concentration is so defined that sulphur trioxide of concentration c'_{SO_3} is in equilibrium with sulphur dioxide of the initial concentration c_{SO_2} and oxygen of the initial concentration c_{O_2}. The actual experimental method by which this process is performed is immaterial. In theory it is always possible. The work w_1 done by the system in this process is due entirely to the change in volume consequent on the disappearance of 3 mols. $(2SO_2+O_2)$ and the production of 2 mols. of SO_3. We have therefore (since in all 1 mol. of gas has disappeared at the temperature T)

$$w_1=-RT.$$

Let the second stage of the process consist of the isothermal expansion (or compression) of the 2 mols. of SO_3 from the concentration c'_{SO_3} to the desired concentration c_{SO_3}. Assuming the validity of the gas laws, we have here, for the work done against the external forces,

$$w_2=2RT\,ln\frac{c'_{SO_3}}{c_{SO_3}}.$$

The total work done is therefore

$$w_1+w_2=2RT\,ln\frac{c'_{SO_3}}{c_{SO_3}}-RT.$$

By definition the affinity A is this maximum amount of work, less the external work necessarily involved in producing the

change in volume. Since the difference in volume between the initial and final gases is equal to the volume of 1 mol., we have

$$A = w_1 + w_2 + RT = 2RT \ln \frac{c'_{SO_3}}{c_{SO_3}}. \quad \ldots\ldots\ldots\ldots\ldots(1)$$

This equation (1) can be subjected to a simple transformation. As c'_{SO_3} is in equilibrium with c_{SO_2} and c_{O_2}, we have, by the law of mass action,

$$c'^2_{SO_3} = K \cdot c'^2_{SO_2} \cdot c_{O_2}.$$

Substituting this in (1), we obtain

$$A = RT \ln \frac{K \cdot c^2_{SO_2} \cdot c_{O_2}}{c^2_{SO_3}} = RT \ln K - RT \ln \frac{c^2_{SO_3}}{c^2_{SO_2} c_{O_2}}. \quad \ldots\ldots(2)$$

Equation (2) gives the affinity tending to cause 2 mols. of sulphur dioxide of concentration c_{SO_2} and 1 mol. of oxygen of concentration c_{O_2} to combine to 2 mols. of SO_3 of concentration c_{SO_3}. The affinity is thus a function of the concentrations, the temperature, and the equilibrium constant. This latter quantity is now capable of a new interpretation. When the concentrations of the reacting substances are all unity, equation (2) reduces to

$$A = RT \ln K, \quad \ldots\ldots\ldots\ldots\ldots(2a)$$

so that the equilibrium constant is a direct measure of the affinity. In the general case of a reaction according to the equation

$$\nu_a A + \nu_b B + \ldots = \nu_m M + \nu_n N + \ldots,$$

(2a) becomes

$$A = RT \ln K - RT \ln \frac{c_M^{\nu_m} \cdot c_N^{\nu_n} \ldots}{c_A^{\nu_a} \cdot c_B^{\nu_b} \ldots}. \quad \ldots\ldots\ldots\ldots(2b)$$

The equations (2) give the variation of the affinity A with the temperature, since the variation of K with the temperature has already been calculated in a former paragraph. Substituting partial pressures for concentrations, we obtain

$$A = RT \ln K' - RT \ln \frac{p_M^{\nu_m} p_N^{\nu_n} \ldots}{p_A^{\nu_a} p_B^{\nu_b} \ldots}. \quad \ldots\ldots\ldots\ldots(2c)$$

Differentiating at constant pressure, *i.e.* under the condition that $p_M^{\nu_m} \dots p_A^{\nu_b} \dots$ all remain constant, we obtain

$$\left(\frac{\partial A}{\partial T}\right)_p = R\,ln\,K' - RT\frac{\partial\, ln\,K'}{\partial T} - R\,ln\frac{p_M^{\nu_m} p_N^{\nu_n} \cdots}{p_A^{\nu_a} p_B^{\nu_b} \cdots},$$

and combining this with (2*c*) and (5*a*) (p. 305), we have

$$\left(\frac{\partial A}{\partial T}\right)_p = \frac{A - Q_p}{T}$$

or

$$A = Q_p + T\left(\frac{\partial A}{\partial T}\right)_p \quad \dots\dots\dots\dots\dots\dots\dots\dots (3)$$

Equation (3) is often called the Helmholtz equation on account of its close relationship with the original Helmholtz equation (Chapter VI. p. 186 (22)). It can be derived directly from equation (21) (p. 186), since $-A$ is the change in the thermodynamic potential and $-Q_p$ the change in the heat content H produced by the isothermal interaction of unit mass in mols. of each of the reacting substances.

This equation demonstrates the falseness of Berthelot's principle (p. 128), which states that the affinity and the heat of reaction are equal to one another. We see further that A and Q_p approach one another as the temperature is diminished to the absolute zero, provided that $\frac{\partial A}{\partial T}$ does not become infinitely great.

We can deduce the above equations directly by means of the thermodynamic potential (see Chapter VI. p. 174).

Writing ζ_1, U_1, S_1; ζ_2, U_2, S_2; etc., for the thermodynamic potential, total energy, and entropy of each of the reacting substances, and $\Sigma\zeta_1 = -A$, $\Sigma S_1 = S$, $\Sigma(U_1 + p_1 v_1) = \Sigma H = -Q_p$,* we have, since $\zeta_1 = U_1 - TS_1 + p_1 v_1$, etc.,

$$+A = +Q_p + TS. \quad \dots\dots\dots\dots\dots\dots\dots\dots (3a)$$

$+A$, the negative change in the thermodynamic potential, is equal to the maximum work obtainable less the work necessarily

* Work ($+A$) is done by the chemical forces when the products of the reaction have a smaller thermodynamic potential than the substances initially present, and heat is evolved in the reaction when they have a smaller value of $U + pv = H$.

done owing to the change in volume of the reacting substances. For perfect gases whose specific heat is constant, we have

$$S_1 = c_v \ln T + R \ln v_1 + S_1',$$

and hence $$A = Q_p + \Sigma c_v T \ln T + RT \Sigma \ln v + T\Sigma S_1'.$$

By equation (4*a*) (p. 302), we have further

$$\frac{Q_p}{T} + \Sigma c_v \ln T + \Sigma S' = R \ln K,$$

and hence $$A = RT \ln K - RT \Sigma \ln c. \quad \ldots\ldots\ldots\ldots\ldots\ldots (2b)$$

Equation (3*a*) is strictly true for all chemical reactions, and is not confined to reactions between perfect gases. The same is true of the Helmholtz equation (3), which may be deduced directly from (3*a*). By equation (12), Chapter VI. p. 184, we have

$$-S_1 = \left(\frac{\partial \xi_1}{\partial T}\right)_p, \text{ and hence } \Sigma \xi_1 = \Sigma(U_1 + p_1 v_1) + T\Sigma\left(\frac{\partial \xi_1}{\partial T}\right)_p$$

or $$A = Q_p + T\left(\frac{\partial A}{\partial T}\right)_p.$$

It is worthy of note that A may be either greater or smaller than Q_p according to the sign of $\frac{\partial A}{\partial T} = S$. The affinity is greater than the heat of reaction when the entropy of the system is increased by the reaction, *i.e.* when $S > 0$. It is less than the heat of reaction when $S < 0$, *i.e.* when the entropy of the system diminishes during the reaction. A reaction of this latter type is not at variance with the second law, which states that the entropy of a system can never diminish, for this statement applies only to isolated systems. In isothermal reactions, for example, heat may be evolved by the system whereby the entropy of the surroundings would be increased.

The quantity $$-(Q_p - A) = T\left(\frac{\partial A}{\partial T}\right)_p = TS = q$$

is the amount of heat which the system absorbs (at constant pressure) when the reaction proceeds reversibly, and yields the maximum amount of work. We may call this quantity the

latent heat of the reaction on account of its close relationship to the quantity * to which Helmholtz gave this name.

When the latent heat of the reaction is positive, the affinity increases with the temperature, and *vice versa*. In most cases the latent heat is negative.

If the reaction is made to yield work without interchange of heat with the surroundings, the temperature of the system will change. There are two cases :

1. $q = A - Q_p$ is positive, *i.e.* the work done is more than equivalent to the heat of reaction. In this case the deficient heat energy is supplied by the system itself, so that the temperature must fall.

2. $q = A - Q_p$ is negative, so that only part of the heat of reaction is used up in doing work. In this case the temperature of the system must rise.

Substituting in (2*b*) the value of $\log K$ given in equation (9), p. 307, we can express A as a function of the temperature, viz.

$$A = Q_0 + \Sigma\nu_a T \ln T + \frac{\Sigma\beta}{2} T^2 + \frac{\Sigma\gamma}{2} T^3 + \ldots + JRT$$

$$+ RT \ln \frac{C_M^{\nu_m} C_N^{\nu_n} \ldots}{C_A^{\nu_a} C_B^{\nu_b} \ldots}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

or, in terms of partial pressures by (9*a*), p. 207, and (2*c*), p. 318,

$$A = Q_{1.0} + \Sigma\nu_a T \ln T + \frac{\Sigma\beta}{2} T^2 + \frac{\Sigma\gamma}{6} T^3 + \ldots + J'RT$$

$$- RT \ln \frac{p_M^{\nu_m} \cdot p_N^{\nu_n} \ldots}{p_A^{\nu_a} \cdot p_B^{\nu_b} \ldots}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4a)$$

where $J' = J + \nu \ln R$.

Using the approximate formula (11*a*) and taking

$$p_M^{\nu_m} = p_N^{\nu_n} = \ldots = p_A^{\nu_a} = p_B^{\nu_b} = \ldots = 1,$$

* Helmholtz gave this name to the change in the quantity $T\left(\frac{\partial\psi}{\partial T}\right)_v$ of equation (22), p. 186. When the volume of the system is not altered by the reaction, the two quantities are identical.

so that the reacting substances are all at 1 atm. pressure, we obtain the approximate equation,

$$A = Q_{p_0} + \Sigma c_p T_0 + \Sigma c_p T \ln T + J'RT, \quad \ldots\ldots\ldots\ldots (4b)$$

while the heat of reaction is given by

$$Q_p = Q_{p_0} - \Sigma c_p (T - T_0). \quad \ldots\ldots\ldots\ldots (5)$$

To illustrate the use of equations (4*b*) and (5), the heat of reaction and the affinity of the formation of water from hydrogen and oxygen have been calculated, and are given in the following table. As on p. 310, we have

$$\Sigma c_p = -5, \quad Q_{p_0} = 116000 \text{ cal.}, \quad J' = 2{\cdot}3J'' = 2{\cdot}3 \times 2{\cdot}8 = 6{\cdot}4,$$

and therefore

$$\begin{aligned} A &= 116000 - 5 \times 373 - 5 \times 2{\cdot}3T \log T + 6{\cdot}4 \times 2T \\ &= 114100 - 11{\cdot}5T \log T + 12{\cdot}8T. \end{aligned}$$

and

$$\begin{aligned} Q_p &= 116000 + 5(T - 373) \\ &= 114100 + 5T. \end{aligned}$$

$T_{abs.}$	A.	Q_p.
500	105000	116600
1000	98500	119100
1500	78500	121600
2000	63800	124100
2500	48400	126600

After subtracting the work necessarily done owing to the change in volume, A is the maximum work which can be done by the chemical forces when 2 mols. of H_2 at atmospheric pressure and 1 mol. of oxygen at atmospheric pressure unite to form 2 mols. of water at atmospheric pressure. A is always smaller than Q_p, as the table shows, and diminishes considerably as the temperature is raised. It is only at relatively low temperatures that A becomes approximately equal to Q_p.

3. Kinetic theory of the law of mass action.

The law of mass action, like many other consequences of thermodynamics, can be deduced from kinetic considerations.

An elementary form of the deduction was given by Pfaundler and others, and may be stated as follows.

A chemical equilibrium is not a statical state of rest in which nothing is happening, but is a dynamical equilibrium in which the two opposite reactions which lead to the equilibrium (*e.g.* the formation and dissociation of water vapour) are proceeding at equal rates.

Thus, in a reaction according to the equation $A+B=C+D$, the velocity of the reaction from left to right will be greater, the more frequently the rapidly moving molecules of A and B collide with one another. It would seem plausible to assume that the velocity v_1 of this reaction is directly proportional to the number of collisions per second, and hence to the product of the concentrations of A and B. Thus we obtain the equation

$$v_1 = k_1 c_a c_b.$$

Similarly, we may assume that the velocity v_2 of the reaction from right to left is proportional to the number of collisions between the molecules of C and D, and hence

$$v_2 = k_2 c_c c_d.$$

Chemical equilibrium will be established when the velocities of the two opposite reactions are equal to one another; in other words, when the same number of molecules of B and C are formed and decomposed in unit time. The condition for the equilibrium is therefore

$$v_1 = v_2 = k_1 c_a c_b = k_2 c_c c_d$$

or

$$\frac{c_c c_d}{c_a c_b} = \frac{k_1}{k_2} = K.$$

Regarded from this point of view, the equilibrium constant is the quotient of the two velocity constants.

While these kinetic considerations give us a picture of the manner in which the equilibrium is established, it is clear that they cannot be regarded as proving the law of mass action. Our hypothesis that the concentrations are proportional to the number of collisions is not immediately justifiable unless the velocities of all similar molecules are equal to one another. In

Chapter V., however, we showed that the molecules of a gas may have an indefinitely large number of different velocities which, according to Maxwell's law of distribution (*i.e.* according to the laws of probability), are grouped about a certain mean value. A strict deduction of the law of mass action must therefore be founded on the laws of probability, by means of which all the other gas laws have been derived. Making certain new assumptions as to the nature of the bonds between the atoms in the molecule, Boltzmann,* and later Jaeger,† Natanson,‡ and Krüger,§ succeeded in deducing by statistical methods, not only the law of mass action, but also the relation between the equilibrium constant, the heat of reaction, and the temperature. The author || has recently shown that these thermodynamical relationships can all be deduced, without any assumptions as to the mechanism of chemical combination, from the fundamental law that every spontaneous chemical reaction like every other irreversible process leads to an increase in the molecular chaos; in other words, that chemical equilibrium is characterised by maximum "probability." The details of these calculations will not be discussed here.

4. Equilibria in solutions.

The laws which we deduced for gaseous systems in the preceding paragraphs apply, as theory and experiment have shown, to reactions in dilute solutions, provided that all the substances present in the solution obey van't Hoff's laws of osmotic pressure with sufficient accuracy.

The law of mass action therefore applies to chemical equilibria between substances in solution in any solvent, and the variation of the equilibrium constant with the temperature is determined by the heat of reaction. The numerical value of the equilibrium constant follows from equations (8) and (9) (p. 307), and is therefore given by the heat of reaction, the specific heats of the reacting substances, and a (thermodynamically)

* *Gastheorie*, ii. p. 177.

† *Wiener Sitzungsberichte*, **100**, 1182 (1891); **104**, 671 (1895).

‡ *Ann. d. Physik*, **38**, 288 (1889).

§ *Nachrichten der Göttinger Akademie* (1908), p. 318.

|| O. Sackur, *Ann. d. Physik* (4), **36**, 958 (1911).

indeterminate constant. All these quantities may depend on the nature of the solvent (which may or may not take part in the reaction) in a manner which cannot as yet be predicted by theory. The position of a chemical equilibrium in solution will therefore depend on the nature of the solvent. Experiment has shown that this is always the case, but the influence on the equilibrium of the chemical and physical properties of the solvent has not yet been elucidated.

Theory of esterification. As was mentioned on p. 298, the experiments of Berthelot and Péan de St. Giles led Guldberg and Waage to the discovery of the law of mass action. The recognition of this law is thus connected historically with the investigation of reactions in solutions. Using the experimental data of Berthelot and Péan de St. Giles to test the constancy of the expression

$$\frac{c_{\text{ester}}c_{\text{water}}}{c_{\text{acid}}c_{\text{alcohol}}} = K,$$

we find, however, that the law is only very roughly obeyed. This is due to the fact that the condition under which alone the law of mass action is strictly valid, namely, great dilution of the solution, was not fulfilled in the experiments. The following table contains the results of the calculation for one of the experiments. Let x mols. of ester result from the interaction of 1 mol. of alcohol and 1 mol. of acid. If a is the number of mols. of ester originally present and v the volume of the solution after equilibrium has been attained, we have

$$c_{\text{ester}} = \frac{a+x}{v}, \quad c_{\text{water}} = \frac{x}{v}, \quad c_{\text{acid}} = c_{\text{alcohol}} = \frac{1-x}{v},$$

and hence, for equilibrium at constant temperature,

$$\frac{(a+x)x}{(1-x)^2} = K.$$

In this case the equilibrium constant is independent of the volume, as the reaction proceeds without change in the number of molecules.

The "constant" K varies considerably, as we see from the table on p. 326. This is clearly due to deviations from van't Hoff's laws in these very concentrated mixtures.

We find a much better agreement with the law of mass action when the reaction takes place in a solvent which does not itself participate in the reaction, and is present in so great excess that the reacting substances are all very dilute.

a.	x_{exp}*	K.
0·05	0·639	3·4
0·13	0·626	3·4
0·43	0·589	3·6
0·85	0·563	4·1
1·6	0·521	4·8

According to Menschutkin, the esters of tertiary alcohols are split up by water into acid and unsaturated hydrocarbons instead of being saponified into the corresponding alcohol and acid. Thus the amyl ester of acetic acid forms acetic acid and amylene according to the equation

$$CH_3COO(C_5H_{11}) = CH_3COOH + C_5H_{10}.$$

This equilibrium was investigated at 100° by Nernst and Hohmann.† If a is the number of mols. of amylene which are mixed with 1 mol. of acid in the volume v and x the number of

a.	v.	x_{exp}	K.
2·15	361	0·762	0·00120
4·12	595	0·814	0·00127
4·48	638	0·820	0·00126
6·63	894	0·838	0·00125
6·80	915	0·839	0·00126
7·13	954	0·855	0·00112
7·67	1018	0·855	0·00113
9·12	1190	0·857	0·00111
9·51	1237	0·863	0·00111
14·15	1787	0·873	0·00107

* Quoted from Guldberg u. Waage, *Ostwalds Klassiker*, No. 104, p. 95, Table 3.

† *Zeitschr. f. physikal. Chemie*, **11**, 352 (1893),

mols. of ester which are formed after the equilibrium has been established, we have

$$c_{\text{amylene}} = \frac{a-x}{v}, \quad c_{\text{acid}} = \frac{1-x}{v}, \quad \text{and} \quad c_{\text{ester}} = \frac{x}{v},$$

and therefore

$$\frac{(a-x)(1-x)}{xv} = K.$$

The table on p. 326 shows the correctness of this equation.

Ostwald's law of dilution. The application of the law of mass action to solutions of electrolytes is of particular interest. Here we have equilibrium between the free ions and the undissociated molecules. For the ionisation of a binary electrolyte AB composed of two univalent ions we have the equation $AB = A' + B'$. At constant temperature the ionic concentrations c_a and c_b must therefore be connected at all concentrations with the concentration c_{ab} of the unionised molecules by the equation

$$\frac{c_a c_b}{c_{ab}} = K.$$

Let c be the total concentration (ions + unionised molecules) which alone can be determined by analysis, and α the degree of ionisation. We have then

$$c_a = c_b = \alpha c,$$
$$c_{ab} = c(1-\alpha),$$

and hence

$$\frac{\alpha^2 c}{1-\alpha} = K.$$

Writing $1/v$ instead of c, where v (the "dilution") is the volume in which 1 mol. of the electrolyte is dissolved, we obtain

$$\frac{\alpha^2}{(1-\alpha)v} = K.$$

The equation in this form is known as Ostwald's law of dilution.

There are two methods of determining the degree of dissociation α. First, the equation $\alpha = \frac{\Lambda_v}{\Lambda}$, where Λ is the equivalent conductivity at the dilution v and Λ_v is the equivalent conductivity at infinite dilution, and, secondly, any of the osmotic methods described in Chapter VIII. (change in freezing point, boiling

point, or vapour pressure of the solution), which enable us to determine the total number of molecules and ions present, *i.e.* the quantity $c(1+\alpha)$. For weak electrolytes, such as most organic acids and bases, which are only slightly dissociated into their free ions, α is a small quantity, so that the second method, which involves the calculation of α from the difference of two nearly equal quantities, cannot give very accurate results. In such cases we have to resort to the conductivity method. The values obtained for α in this way agree excellently with Ostwald's law for widely varying concentrations up to about $\frac{1}{2}$ normal. The equilibrium constant K was termed by Ostwald the dissociation constant of the acid or base. It is a quantitative measure of the "avidity" or strength of the acid or base as the chemical activity of the acid or base is solely determined by the concentration of the free $H^{\cdot}$ or OH' ions, and this is measured by the equilibrium constant.

For strong electrolytes, such as the strong acids and bases and neutral salts, the law of dilution is valid only in very dilute solutions (less than 1/1000 normal). In concentrated solutions the "constant" always varies, in general increasing with concentration.

The calculation of the degree of dissociation by the two methods mentioned above leads to different values, so that at least one of them must be false, or rather based on false assumptions. The discrepancy may be accounted for by assuming that the simple laws of van't Hoff are not applicable to the free ions. The law of mass action would then no longer be valid for equilibria between ions and undissociated molecules, and apart from this the osmotic methods of calculating the ionic concentrations would no longer be strictly accurate.

The free ions of weak electrolytes, even in relatively concentrated solutions, are present in such small quantities that they still conform to the simple laws. It is possible that the free electric charges on the ions exert appreciable forces on one another in concentrated solutions. This would cause deviations from the simple laws analogous to the deviations from the simple gas laws which are accounted for by van der Waals' theory.

In solutions of strong electrolytes the equilibrium between

the free ions and the undissociated molecules must therefore be represented by an equation differing from Ostwald's. Several different equations have been proposed by various investigators, partly empirical and partly deduced from definite hypothesis. Thermodynamical methods cannot decide between these various equations, as the determination of the equation of state of dissolved substances is beyond the bounds of thermodynamics, which merely enables us to determine the connection between the equation of state and the equilibrium law. For this reason we shall refrain from a further discussion of the various dissociation laws for strong electrolytes.

Variation with the temperature. The equilibrium constant in solutions as in gases is a function of the temperature. When van't Hoff's osmotic pressure laws are applicable, we can deduce an equation of the form

$$ln\, K = \frac{Q_0}{RT} + \frac{\Sigma c_{v_0}}{R} ln\, T + \frac{\Sigma \beta}{2R} T + \ldots + J,$$

analogous to that obtained for gases ((9), p. 307). This equation is, however, valueless in practice. It is impossible to determine the constants Σc_{v_0}, β, γ, ... in the specific heat equation with sufficient accuracy to justify our calculating the integration constant from them. This is due to the narrow range of temperature (between the freezing and boiling points) in which a solution can exist at all. We can therefore utilise for solutions only the differentiated equation (5), p. 304, which gives the direction of the change in the equilibrium with temperature as a function of the heat of reaction, viz.

$$\frac{d\, ln\, K}{dT} = -\frac{Q}{RT^2},$$

or, integrated for a small range of temperature,

$$ln \frac{K_2}{K_1} = -\frac{Q}{R} \frac{T_2 - T_1}{T_1 . T_2}.$$

Owing to the smallness of the range of temperature in which solutions are stable, this equation is often approximately valid for all temperatures at which the solution can exist.

We can employ this equation to calculate the heat of reaction in cases where the direct experimental determination is difficult. Arrhenius calculated the heat of ionisation of electrolytes in this way. The equation shows that the degree of dissociation increases with temperature when heat is evolved ($Q>0$) in the dissociation of the dissolved electrolyte molecules into their free ions, and *vice versa*. Petersen * calculated the heat of dissociation of a number of acids in this way and obtained the following values :

	Dilution (litres per mol.).	Q_{exp}	Q_{calc}
HF - - -	5–10	111	116
CCl_2HCOOH - -	2–4	262	286
H_3PO_4 - - -	2–4	72	100
H_3PO_2 - - -	4–8	340	371

The figures under $Q_{exp.}$ were determined calorimetrically.

The law of mass action is not accurately obeyed by concentrated solutions of strong electrolytes, so that their heat of dissociation cannot be calculated in this way.

We may, however, conclude from the invariable decrease in the dissociation with rising temperature, observed by Noyes and his collaborators, that the splitting up of the molecules of strong electrolytes into their free ions is accompanied by evolution of heat. This is a remarkable result, as the purely thermal dissociation of complex molecules into simpler molecules or atoms is usually accompanied by absorption of heat.

If the liquid acting as solvent takes part in the reaction (as in the saponification of esters by water in presence of a large excess of water), the above equations remain valid notwithstanding the fact that one of the reacting substances is not in the state of great dilution demanded in the derivation of the equations. For, in this case, the concentration of the solvent remains practically constant throughout the reaction (provided that the other reacting substances are sufficiently dilute), and

* *Zeitschr. f. physikal. Chemie*, **11**, 174 (1893).

may therefore be included in the equilibrium constant. Thus, for the saponification of ethyl acetate, according to the equation

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH,$$

the law of mass action assumes the form

$$\frac{c_{\text{alcohol}}\, c_{\text{acid}}}{c_{\text{ester}}} = K.$$

If the solution is very dilute, the concentration of the solvent in the solution has the same value as in the pure solvent $\left(e.g. \frac{1000}{18} = 55{\cdot}5 \frac{\text{mols.}}{\text{litre}} \text{ for water}\right)$. In slightly more concentrated solutions the concentration of the solvent is somewhat smaller than this, and may be taken to be proportional to the vapour pressure of the solvent in the calculation of the equilibrium constant. The concentration of the solvent calculated in this way from the proportionality to the vapour pressure is called by Nernst the active mass of the solvent. The active mass is, however, only strictly proportional to the vapour pressure when the solution obeys Raoult's law for the lowering of the vapour pressure. In Chapter VIII. we showed that this is the case in dilute solutions, which obey the laws of van't Hoff.

An important application of the above considerations is the calculation of the dissociation of water into the ions $H^{\cdot}$ and OH' according to the equation

$$H_2O = H^{\cdot} + OH'.$$

By the law of mass action we have in this case

$$H^{\cdot} \times OH' = K.$$

This equation must hold in all aqueous solutions for all values of the $H^{\cdot}$ and OH' concentrations. As the concentration of the $H^{\cdot}$ ions is very considerable in acid solutions and exceedingly minute in alkaline solutions, we have here a means of testing the law of mass action over a much greater range of concentration than was available in any of the other cases at our disposal. We need not enter into the discussion of the various independent methods which have been employed in the calculation of the dissociation of water in acid, neutral, and alkaline

solutions. They all give results in excellent agreement with the law of mass action.

The change in the dissociation of water with the temperature is also in agreement with the theory. According to the latest experiments of Noyes, Kato, and Sosman* on the hydrolysis of ammonium acetate at high temperatures, the dissociation constant of water increases rapidly with the temperature. This is shown by the following table:

$t°$.	$K \times 10^{14}$.	$Q_{calc.}$	$Q_{exp.}$
0	0·088	14500	14700
18	0·46	13800	13400
25	0·81	13000	
50	4·5	11800	
75	16·9	10700	
100	48	9220	
128	114	7850	
156	217	—	

The first column contains the temperature in degrees centigrade, the second the experimental values of K, and the third the heat of dissociation calculated by van't Hoff's equation. The fourth column contains the values of the heat of neutralisation of strong acids and bases determined calorimetrically by Wörmann.†

By paragraph 5, Chapter IV., this is identical with the heat of dissociation of water.

The agreement at low temperatures is remarkably good. The heat of dissociation diminishes as the temperature rises. From this it follows that the free ions $H^{\cdot}$ and OH' must have a smaller specific heat than the unionised molecules. The calculation of the ionisation of water is one of the most convincing proofs of the correctness of the theory of electrolytic dissociation, as well as of the validity of van't Hoff's osmotic pressure laws on which the deduction of these valuable equations is based.

* *Zeitschr. f. physikal. Chemie*, **73**, 1 (1910).
† *Annalen d. Physik* (4), **18**, 793 (1905).

5. Reactions in heterogeneous systems.

Reactions between gases and solids. We shall now remove the restriction imposed in paragraph 1, p. 297, namely, that all the reacting substances shall belong to the same phase; and shall consider reactions between substances in different states of matter. Let us first consider the simplest case of a reaction between solids and gases.

Examples of such gaseous-solid reactions are comparatively common, and the fact that they are susceptible of simple thermodynamical treatment was discovered relatively early.* Many solid compounds dissociate when the temperature is raised, giving off one or more gases. Examples of this are: calcium carbonate, according to the equation

$$CaCO_3 = CaO + CO_2 ;$$

salts containing water of crystallisation, such as

$$CuSO_4 . 5H_2O = CuSO_4 + 5H_2O ;$$

ammonia complex salts, such as

$$AgCl . 2NH_3 = AgCl + 2NH_3 ;$$

oxides of heavy metals, such as

$$Ag_2O = 2Ag + \tfrac{1}{2}O_2 ;$$

and, finally, the classical example of all reactions of this type, ammonium chloride according to the equation

$$NH_4Cl = NH_3 + HCl.$$

Besides these there are a large number of reactions which are of great importance in the preparation of chemical substances and in technical chemistry, such as the reduction of metallic oxides by carbonic oxide, the action of water vapour on carbon or on metals, etc. It is, therefore, not surprising that reactions between solids and gases have been investigated so thoroughly both theoretically and experimentally in the last few decades.

We shall place at the head of the following thermodynamical discussion the almost obvious theorem that the vapour pressure

* Horstmann, *Berichte d. Deutsch. chem. Gesellsch.* 1869, 137; *Ostwald's Klassiker*, No. 137.

of all solids, as of all liquids, has a finite value at every temperature, which, however, may sometimes be exceedingly minute. It follows at once from this, by the phase rule, that the vapour pressure is a function of the temperature alone. It is also a perfectly general rule that the vapour pressure increases with the temperature. We are justified in postulating the existence of the vapour pressure at low temperatures, even when it is too small to be actually measured, as nearly all solids which do not previously decompose can be made to evaporate by increasing the temperature sufficiently.

We may now regard every reaction between solids and gases as taking place in a series of steps, namely, first, evaporation of the solids at their vapour pressure; second, chemical transformation of the vapours formed; and, finally, condensation of the products to the solid state, in so far as solids are formed by the reaction. Thus the dissociation of $CaCO_3$ may be assumed to take place as follows: (1) Isothermal vaporisation of solid $CaCO_3$ to $CaCO_3$ vapour at the partial pressure p_{CaCO_3} corresponding to the vapour pressure of $CaCO_3$ at the temperature T. (2) Dissociation of the $CaCO_3$ vapour into gaseous CO_2 at the partial pressure p_{CO_2} and CaO vapour of partial pressure p_{CaO} corresponding to the vapour pressure of solid CaO at the temperature T. (3) Condensation of CaO.

The whole system will be in equilibrium when equilibrium has been established for all three steps. In (1) and (3) the condition for equilibrium is given by our fundamental hypothesis. In (2) the condition for equilibrium between the three gases $CaCO_3$ vapour, CO_2 and CaO vapour is such that their concentrations or partial pressures have the values demanded by the law of mass action, namely, those given by the equation

$$\frac{p_{CO_2} p_{CaO}}{p_{CaCO_3}} = K.$$

p_{CaO} and p_{CaCO_3} are vapour pressures of solids, and therefore functions of the temperature alone. At constant temperature they are constants, and we may therefore write $p_{CO_2} = K'$. The pressure of CO_2, which is in equilibrium with solid CaO and

$CaCO_3$, has therefore a definite constant value for each temperature, and is independent of the proportions of the two solids in the mixture. It follows from this that the dissociation of $CaCO_3$ proceeds at constant temperature until the pressure of CO_2 has attained this equilibrium value. This equilibrium pressure is usually called the dissociation pressure. We can treat dissociations of this kind, in which there is only one gaseous product of the reaction, in the same way as the vaporisation of a single substance.

The law of mass action is also immediately applicable to reactions in which several gaseous substances are formed.

Thus, for the action of water vapour on carbon, according to the equation

$$H_2O + C = CO + H_2,$$

we have at every temperature the equation

$$\frac{p_{CO}\, p_{H_2}}{p_{H_2O}\, p_C} = K,$$

or as p_C, the vapour pressure of solid carbon, is independent of the concentration,

$$\frac{p_{CO} \cdot p_{H_2}}{p_{H_2O}} = K'.$$

We see therefore that the condition for equilibrium in a reaction between solids and gases is obtained by applying the law of mass action to the reaction between the gaseous substances in the system. The presence of solids influences the numerical value of the equilibrium constant, but not the form of the equilibrium equation.

We may illustrate the application of these considerations to technical chemistry by the "water gas" equilibrium. The conversion of a definite amount of carbon into the combustible gases CO and H_2 can only be carried to completion when the product of the partial pressures of the CO and H_2 formed, divided by the partial pressure of the water vapour, is equal to or less than the equilibrium constant K' at the temperature of the reaction. For it is only under these conditions that the formation of CO and H_2, that is, the increase in the product $\frac{p_{CO} p_{H_2}}{p_{H_2O}}$, can proceed.

If the reaction is carried out in a closed vessel, the conversion is not complete, as the partial pressures of the gases formed would attain very large values if any considerable quantity of carbon were transformed. If the carbon is heated in a current of water vapour, the gases are removed as fast as they are formed, so that their partial pressure at the surface of the carbon is maintained at a small value. In this way only is the complete conversion of the carbon into "water gas" possible. Currents of gases are employed in a similar manner in the decomposition of calcium carbonate (the burning of lime) and in the reduction of ores by carbon monoxide. This procedure is used extensively in technical processes.

Change in the equilibrium with temperature. We have deduced the expression

$$\frac{p_{CO}\,p_{H_2}}{p_{H_2O}} = K' = Kp_C$$

for the equilibrium between carbon and water vapour. The equilibrium constant K' can be determined empirically, while K and p_C cannot be measured directly. The variation of K and p_C with the temperature can, however, be deduced without difficulty. K is the equilibrium constant of a reaction between gases alone, while p_C is the vapour pressure of a solid. Hence, if Q be the heat of reaction (at constant pressure) in the gaseous system and L the latent heat of carbon, we have the equations

$$\frac{d\,ln\,K}{dT} = -\frac{Q}{RT^2}$$

and

$$\frac{d\,ln\,p_C}{dT} = -\frac{L}{RT^2}.$$

None of the quantities involved in these two equations can be determined by experiment. Adding, however, we obtain

$$\frac{d\,ln\,Kp_C}{dT} = \frac{d\,ln\,K'}{dT} = -\frac{Q+L}{RT^2} = \frac{-Q'}{RT^2}. \quad \ldots\ldots\ldots\ldots(1)$$

$Q' = Q + L$ is the heat evolved when 1 mol. of carbon is converted into vapour and then allowed to react with water vapour. Q' is therefore the heat of the reaction between solid carbon

and water vapour as measured in the calorimeter. The form of the relation between the equilibrium constant of a heterogeneous reaction and the temperature is therefore the same as for a reaction in a homogeneous system.

Equation (1) can be tested experimentally by integrating over a small range of temperature, in which we may assume the heat of reaction to be constant. Thus we obtain

$$ln \frac{K_1'}{K_2'} = \frac{Q'}{R} \frac{T_2 - T_1}{T_1 T_2}.$$

If only one gas results from the reaction, as in all simple dissociations, we have $K' = p$, where p is the dissociation pressure. From the values of p determined by experiment we can calculate the heat of reaction $Q'_{\text{calc.}}$ and compare it with the value of $Q_{\text{exp.}}$ measured calorimetrically.

The dissociation of calcium carbonate has been carefully measured of late by Johnston * and Riesenfeld. Johnston's figures are given in the following table :

$t°$.	T.	p (mm. Hg.).	$-Q'_{\text{calc.}}$	$-Q'_{\text{exp}}$
671	944	13·5	—	—
711	984	32·7	41200	43000 cal. at
748	1021	70	40700	0° C.
819	1092	235	37100	(Thomsen and
894	1167	716	37400	de Forcrand)

The agreement with the calorimetrical value is excellent, considering that a temperature error of 1-2° affects the calculated value of Q by 1-2000 cal., and, further, that the heat of reaction diminishes as the temperature is raised.

In applying these equations to actual cases, we must remember that agreement between theory and experiment can only be expected if the assumptions on which the equations are based are justified in the case under consideration. This is not always

* Johnston, *Journ. Amer. Chem. Soc.* **32**, 938 (1910); Riesenfeld, *Journ. de chim. phys.* **7**, 561. Riesenfeld's determinations (possibly owing to experimental errors) give values of Q which increase from 27000 to 33000 between 700° and 950°, and are therefore in disagreement with the calorimetrical determination.

the case for reactions between solids and gases, as the various solid substances may form solid solutions with one another at high temperatures, or may absorb gases if the surface of contact is large * (see Chapter XII.).

When the equations are applicable, the affinity between solids and gases can be calculated very simply. As was explained on p. 316, it is sufficient for this purpose to calculate the work which can be obtained by making the reaction take place in any reversible manner. Thus the affinity between calcium oxide and gaseous carbon dioxide at partial pressure P can be calculated as follows. Let the carbon dioxide be compressed or expanded reversibly at the temperature T for which we wish to calculate the affinity, until its pressure is equal to the partial pressure p which is in equilibrium with solid CaO and $CaCO_3$ at this temperature. The work obtained in this process is $RT\ ln\frac{P}{p}$ (per mol.). Now let 1 mol. of CO_2 combine with CaO at constant pressure. Neglecting the difference in volume between CaO and $CaCO_3$, the work done in this process is RT. The total work obtained is therefore

$$RT\ ln\frac{P}{p} - RT.$$

The affinity is defined as the maximum work obtainable less the work necessarily done (at constant pressure) owing to the change in volume. Hence the affinity between solid CaO and gaseous carbon dioxide of pressure P is given by

$$A = RT\ ln\frac{P}{p}.$$

Counting the pressures in atmospheres and taking the CO_2 initially at a pressure of 1 atmosphere, we obtain

$$A = -RT\ ln\ p. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Combination of CaO and CO_2 at atmospheric pressure can only take place at temperatures at which A is positive, that is to say, at which the dissociation pressure of $CaCO_3$ is less than 1.

* Le Chatelier, *Zeitschr. f. physikal. Chemie*, **69**, 90 (1910).

In the general case of a reaction in which several gaseous substances take part, we obtain in a similar manner the equation

$$A = -RT\,ln\frac{p_A^a p_B^b \cdots}{p_M^m p_N^n \cdots} + RT\,ln\frac{P_A^a P_B^b \cdots}{P_M^m P_N^n \cdots},$$

or, supposing all the gases formed or destroyed by the reaction to be at a pressure of 1 atmosphere,

$$A = -RT\,ln\,K'. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

The equations for the affinity between solids and gases are thus of exactly the same form as for gases alone. As mentioned above, there are a great many reactions between elements and compounds which lead to such heterogeneous reactions, so that this subject is of special importance for the theory of affinity.*

Reactions between solids and solutions may be treated in a similar manner. Every solid has a definite solubility in every solvent, just as it has a definite vapour pressure at a given temperature. The solubility depends on the nature of the solvent and on the temperature, but is independent (in dilute solutions at least) of the presence of other dissolved or undissolved substances. So-called insoluble substances differ from soluble substances only in that their solubility is exceedingly small.

When several solid substances react with one another in presence of a solvent, the condition for equilibrium may be obtained as follows. In homogeneous solutions which contain definite, although possibly very minute, concentrations of all the molecules taking part in the reaction, the law of mass action will hold, provided that the concentrations are not too high. At constant temperature, however, the concentrations of all the substances which are present in the solid state are determined by their solubilities. The constant values of these concentrations may therefore be included in the equilibrium constant, like the vapour pressures of the solid substances in the calculations of the previous paragraph. For reactions between solids and solutions the law of mass action therefore assumes the same form as for homogeneous solutions, viz.

$$\frac{c_A^a c_B^b \cdots}{c_M^m c_N^n \cdots} = K, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

* See Sackur, *Die chemische Affinität*, p. 51 *et seq.*

with the sole difference that the variable concentrations c include only those molecular types with respect to which the solution is not saturated.

As an illustration of this, let us take the ionisation of a sparingly soluble salt (saturated solutions of soluble salts are not sufficiently dilute to permit of the application of the simple laws of solution).

The ionisation of thallous chloride takes place according to the equation

$$TlCl = Tl^{\cdot} + Cl'.$$

As the concentration of the unionised TlCl in the saturated solution has a constant value at each temperature, the law of mass action for the homogeneous solution, viz.

$$(Tl^{\cdot})(Cl') = K(TlCl),$$

reduces to

$$(Tl^{\cdot})(Cl') = L.$$

This new constant L is called the solubility product. The solution as a whole must be electrically neutral, so that

$$(Tl^{\cdot}) = (Cl') = \sqrt{L},$$

provided no other salts are present. For very sparingly soluble salts we may assume the ionisation to be complete, so that the total concentration c, *i.e.* the solubility, is equal to the ionic concentration. The solubility product is therefore equal to the square of the concentration of the saturated solution, *i.e.* $c^2 = L$.

On the other hand, if the solution contains a concentration c' of another salt which has an ion in common with thallous chloride (*e.g.* potassium chloride), we have again $(Tl^{\cdot})(Cl') = L$, but we can no longer write $(Tl^{\cdot}) = (Cl') = c$, for we have now $(Tl^{\cdot}) = c$, $Cl' = c + c'$, and hence $c(c + c') = L$.

The saturation concentration c is therefore less than it was in the pure solvent, and becomes smaller the greater we make c'. The influence of the addition of a salt with a common ion on the solubility was first deduced from the law of mass action and experimentally confirmed by Nernst.*

Another example which has been the subject of numerous investigations is the double decomposition of barium sulphate

* *Zeitschr. f. physikal. Chemie*, **4**, 372 (1889).

by sodium carbonate in aqueous solution, according to the equation

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4.$$

As the solution is saturated with respect to the two "insoluble" salts $BaSO_4$ and $BaCO_3$, equilibrium will be established when $\frac{Na_2SO_4}{Na_2CO_3} = K$. The reaction from left to right in the above equation will therefore proceed farther the greater we make the initial concentration of the sodium carbonate.

It is not as yet possible to test the law of mass action numerically in this case, as the dissociation of ternary electrolytes in concentrated solutions is not accurately known.

The variation of the equilibrium constant with the temperature is again determined by the heat of reaction, according to the equation

$$\frac{d\,ln\,K}{dT} = -\frac{Q}{RT^2}.$$

The derivation of this equation differs so little from those of similar equations which we have already discussed that it need not be repeated here.

Equation (4) illustrates the application of the phase rule to equilibria between solids and solutions. Thus the number of variable concentrations in the equilibrium equation is exactly equal to the degrees of freedom f of the system, namely; the total number n of the molecular types taking part in the reaction less the number B of the substances present in the solid phase ($f = n - B$).* n is also the number of the independent components of the system, which is equal to the total number of molecular types present (n+solvent), less the number of the chemical equations (1). The number of phases is $P = B + 2$ (solution and vapour). Hence

$$f = n - B = n - P + 2,$$

a result to which the phase rule also leads us (Chapter VII. p. 196).

* Ordinarily one would choose the temperature (or equilibrium constant) and $n - B - 1$ concentrations as arbitrarily variable degrees of freedom, instead of the $n - B$ concentrations.

CHAPTER X.

THERMODYNAMICS AND ELECTROCHEMISTRY.

1. Electromotive force and heat of reaction: the equation of Helmholtz.

In galvanic cells we have a means of converting chemical into electrical energy. Thus, if we immerse a rod of zinc and a rod of copper into solutions of zinc sulphate and copper sulphate, and connect the two rods with a metal wire, an electric current will flow through the wire, and at the same time zinc will be dissolved and an equivalent amount of copper will be deposited on the copper rod. Thus the reaction

$$Zn + CuSO_4 = Cu + ZnSO_4$$

takes place in the cell, while the forces of chemical affinity which cause the reaction to proceed produce an electric current. The electrical work done by the cell must therefore be related quantitatively to the change in the chemical energy.

The electrical work which the cell does can easily be measured. According to the experiment of Joule (Chapter III. p. 18) an electric current J passing through a resistance w for the time t produces an amount of heat J^2wt. By Ohm's law $Jw = E$ (the electromotive force between the two ends of the resistance, *i.e.* at the terminals of the cell) and also $Jt = F$, that is, the amount of electricity which flows through the resistance w in the time t. The quantity of electricity F is therefore capable of doing the amount of work FE. By Faraday's laws the amount of electricity F taken from a galvanic cell or passed through an electrolyte is proportional to the number of gram equivalents which react at

the electrodes. Thus a constant quantity of electricity $n \times 96540$ coulombs (where n is the number of equivalents in 1 mol.) is produced when 1 mol. of the reacting substances are used up in the cell (in the above case $n = 2$, as Cu and Zn are bivalent). Taking 96540 coulombs as the electrochemical unit of electrical charge, every reaction capable of producing a current of electricity will yield n units of electricity and nE units of electrical energy per mol., where E is the potential difference between the terminals of the cell.

By the principles of thermodynamics discussed in Chapter V., a galvanic cell will yield the maximum amount of work when the production of electricity takes place reversibly, that is to say, when the changes which take place both inside and outside the cell are completely reversed when an equally strong current is sent in the opposite direction through the cell. This can only occur when the current flowing through the cell is infinitely small, so that the irreversible production of " Joule " heat inside the cell is avoided. The electrode potential of the cell on open circuit (measured by the compensation method, for example) is therefore a measure of the maximum electrical work which the cell can do. It is also a measure of the chemical affinity of the reaction as defined on p. 318, Chapter IX.

Formerly it was assumed that the electromotive force of a galvanic cell, and also the chemical affinity, could be calculated directly from the heat of reaction. W. Thomson and Helmholtz stated this as a consequence of the law of the conservation of energy in the form $nE = Q$. In the case of the Daniel cell this equation was found to be in agreement with experiment. The electromotive force of a Daniel cell was found to be 1·09 volts. The maximum electrical energy which can be obtained by the interaction of 1 mol. of $Zn + CuSO_4$, as calculated by this equation, is therefore $2 \times 1{\cdot}09 \times 96540$ volt coulombs $= 2 \times 1{\cdot}09 \times 9654 \times 0{\cdot}24$ cal.* $= 50000$ cal. approximately, and this is nearly the same as the heat of the reaction

$$Zn + CuSO_4 = Cu + ZnSO_4$$

* A current of 1 ampere produces in a resistance of 1 ohm the amount of heat 0·24 cal. per second. This quantity is called the electrical equivalent of heat.

determined calorimetrically. Later on, however, other cells were found which showed considerable deviations, so that Gibbs and Helmholtz were led to a revision of the Thomson equation in the light of the second law of thermodynamics.

From what has been said in Chapter VI., it is clear that it is by no means always possible to convert the whole of the heat set free in an irreversible process into mechanical or electrical work by causing the process to take place reversibly and isothermally. By doing so we obtain only the change in the thermodynamic potential, while the determination of the heat of reaction gives us the change in the heat content H. By p. 320, we have

$$\Sigma\xi = \Sigma H + T\Sigma\frac{\partial\xi}{\partial T}.$$

The maximum electrical work nE which the cell is capable of doing at constant pressure is equal to the change in the thermodynamic potential, produced by the interaction of 1 mol. of the current producing substances in the cell. Similarly the heat of reaction (at constant pressure) is equal to the corresponding change in the heat content H. We have therefore

$$nE = Q_p + nT\frac{dE}{dT}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

nE is greater or less than Q_p, according to the sign of the temperature coefficient of the electromotive force $\frac{dE}{dT}$. If E increases with the temperature, we obtain more work than is equivalent to the heat evolved by the reaction. Hence the quantity of heat $q = nT\frac{dE}{dT}$ must be supplied to the cell in order to keep its temperature constant, and the temperature will fall if the cell is made to yield current adiabatically. On the other hand, if $\frac{dE}{dT}$ is negative, the quantity of heat $q = nT\frac{dE}{dT}$ is produced in the cell, which would therefore become warmer if allowed to deliver current adiabatically.

Thus, yielding current adiabatically tends to diminish the electromotive force of the cell in every case. This result may be obtained qualitatively from Le Chatelier's principle (p. 208).

The quantity $q = nT\frac{dE}{dT}$ is equal to the heat produced in the cell, and was called by Helmholtz the latent heat.

The Helmholtz equation was confirmed experimentally by Jahn,* and somewhat later by Bugarsky.† Their results are given in the following table.

The values for the Daniel cell are taken from the latest and most accurate measurements of Cohen, Chattaway, and Tombrok‡ In dilute solutions the Daniel cell has a very small temperature coefficient, so that nE is nearly equal to Q. This accounts for the apparent confirmation of the old erroneous equation $Q = nE$. It is important to note that the Helmholtz equation is strictly accurate, as it depends solely on the two laws of thermodynamics. It is, of course, only applicable to reversible cells.

Description of cell.	E in volts at 0°.	nE in cal.	Q_p cal.	$\frac{dE}{dT}$ volt / degree	$nT\frac{dE}{dT}$ cal.	$nE - Q$ calc.
Zn | $ZnSO_4$ sat. - - Cu | $CuSO_4$ sat. - -	1·0934 (15°)	50400	55200	$-4{\cdot}3 \times 10^{-4}$	−5690	−4800
Cu | $Cu(C_2H_3O_2)_2$ aq. - Pb | $Pb(C_2H_3O_2)_2 100 H_2O$	0·4764	21960	16520	$+3{\cdot}85 \times 10^{-4}$	+4840	+5440
Ag | AgCl - - - Zn | $ZnCl_2$, $5H_2O$ - -	1·0171	46900	49080	$-2{\cdot}1 \times 10^{-4}$	−2640	−2190
Ag | AgBr - - - Zn | $ZnBr_2 25H_2O$ - -	0·84095	38770	39940	$-1{\cdot}06 \times 10^{-4}$	−1330	−1160
Hg | Hg_2Cl_2KCl - - Hg | Hg_2O . KOH - -	0·1483	7570	−3280	$+8{\cdot}37 \times 10^{-4}$	−11280	−10950

2. Electromotive force and chemical equilibrium.

The electromotive force of a galvanic cell is a measure of the electrical work which can be obtained from the reaction in the cell. The total or maximum work which can be obtained from the cell reaction includes also the work which is done against the external forces owing to the changes in volume (formation of gas, etc.) of the reacting substances. From the definition of affinity (p. 318) it follows, therefore, that the electromotive

* *Wied. Ann.* **28**, 21 (1886); **50**, 189 (1893).

† *Zeitschr. f. anorg. Chemie*, **14**, 145 (1897).

‡ *Zeitschr. f. physikal. Chemie*, **60**, 706 (1907).

force of the cell is a measure of the affinity. In Chapter IX. we showed that the affinity can be calculated for all reactions in solutions, provided that the simple laws of solution are applicable and the equilibrium constants of the reactions can be determined. When this is the case, the E.M.F. of the cell can be calculated from the concentrations of the reacting substances.

The relationship between chemical equilibrium and the electromotive force of galvanic cells was first recognised by van't Hoff in 1886. It was not until much later, however, that a cell in chemical equilibrium was investigated experimentally, as it is not easy to find cells in which the equilibrium is not entirely to the one side or the other. In most cells the reaction and the production of current proceed until one of the reacting substances has disappeared almost entirely (*e.g.* the precipitation of copper by zinc in the Daniel cell). At the instigation of Bredig, Knüpffer* investigated a cell made up as follows :

Thallium amalgam.	KCl solution saturated with TlCl.	KCNS solution saturated with TlCNS.	Thallium amalgam.

When a positive current is sent through the cell in the direction from left to right, thallium goes into solution at the chloride electrode, and a corresponding amount of thallous chloride is precipitated, while thallous thiocyanate is decomposed and a corresponding amount of metallic thallium is deposited at the other electrode. The reaction in the cell may therefore be represented by the equation

$$\underset{\text{solution}}{KCl} + TlCNS = TlCl + \underset{\text{solution}}{KCNS}.$$

If the concentrations are so chosen that this reaction would take place spontaneously, the cell will produce a current in the direction stated above. On the other hand, if the concentrations are taken so that the affinity is in the opposite direction, the cell will give a current in the reverse direction.

By Chapter IX. the affinity of the reaction for dilute solutions is given by

$$A = RT \ln K - RT \ln \frac{[KCl]}{[KCNS]}$$

* *Zeitschr. f. physikal. Chemie*, **26**, 255 (1898).

(since TlCl and TlCNS are present in the solid state, and their constant saturation concentrations can be included in the equilibrium constant).

K is the equilibrium constant, which Knüpffer determined chemically by shaking solutions of KCl and KCNS with solid TlCl and TlCNS at different temperatures. As thallium is a monovalent element, we have $n = 1$, and hence

$$E = A = RT \ln K - RT \ln \frac{[\mathrm{KCl}]}{[\mathrm{KCNS}]}. \quad \ldots\ldots\ldots\ldots (2)$$

Knüpffer's results are given in the following table :

$t°$.	[KCl] : [KCNS]	$K_{exp.}$	E_{exp}	E_{calc}
39·9	0·83	0·85	+0·0010	+0·0006
—	1·50	—	−0·0141	−0·0153
20·0°	0·84	1·24	+0·0105	+0·0098
—	1·52	—	−0·0048	−0·0052
0·8	0·84	1·74	+0·0175	+0·0171
—	1·55	—	+0·0037	+0·0027

The E.M.F. of the hydrogen oxygen cell, viz.

Pt charged with H_2 | H_2O | Pt charged with O_2,

can be calculated in a similar manner. The cell gives a current from left to right (within the cell), while chemical reaction takes place according to the equation $2H_2 + O_2 = 2H_2O$. The E.M.F. is therefore given by the equation

$$E = \frac{RT}{4} \ln K - \frac{RT}{4} \ln \frac{p^2_{H_2O}}{p^2_{H_2} \times p_{O_2}},$$

where p_{H_2O}, p_{H_2}, and p_{O_2} are the partial pressures of the gases over the solution, and the equilibrium constant also refers to the gaseous phase. It is immaterial for the calculation whether we suppose the reaction to take place in the gas or in the solution, as the maximum work obtainable and hence also the affinity are independent of the manner in which the reaction proceeds.

In order to calculate the E.M.F. of this cell, we must therefore know the dissociation constant of water vapour at room temperature. This cannot be determined by direct analysis, as the dissociation is too slight at low temperatures. Nernst and v. Wartenberg * extrapolated from the values of the dissociation constant at higher temperatures by means of the thermodynamical equation on p. 310, and find in this way for the E.M.F. of the hydrogen-oxygen cell at 17° a value of 1·232 volts. Actual determinations by various observers give lower values, the highest of which is 1·14 volts. As the calculation is probably fairly accurate, we must conclude that the assumptions on which it is based were not fulfilled in the experiments. The facts seem to indicate that the oxygen electrode of the cell is not reversible, so that the chemical change accompanying the production of current is not completely reversed when water is electrolysed. It is possible that platinum and oxygen unite irreversibly to form an oxide of platinum which is reduced with formation of water when the cell is in action.†

Haber and others determined the E.M.F. of the hydrogen-oxygen cell at high temperatures, using glass or porcelain as electrolytes.‡ In agreement with theory the E.M.F. diminishes considerably with the temperature. The difference between the calculated and observed values becomes less and less as the temperature is raised, so that the oxygen electrode apparently becomes more nearly reversible at high temperatures.

Measurements of the electromotive force of cells may be used conversely to determine equilibria which are not otherwise amenable to experiment. This method is very frequently employed. The thermodynamical relationship between the electromotive force and the equilibrium constant is often a very convenient means of determining equilibria which cannot be investigated directly at low temperatures owing to the slow rate at which the reactions proceed. As we have seen in the case of the hydrogen-oxygen cell, this method is only applicable when the

* *Zeitschr. f. physikal. Chemie*, **56**, 534 (1906).

† See also the calculation of the E.M.F. of the hydrogen-oxygen cell by G. N. Lewis, *Zeitschr. f. physikal. Chemie*, **55**, 465 (1906).

‡ *Zeitschr. f. anorg. Chemie*, **51**, 245, 289, 356 (1906).

cell under investigation is strictly reversible. As yet, however, we have no infallible criterion of reversibility. In many cases the Helmholtz equation (p. 344) is a valuable test. If the heat of reaction calculated from the E.M.F. and its temperature coefficient agrees with the calorimetrical determination, there is a certain amount of probability in favour of the reversibility of the cell. This criterion may, however, also fail. The hydrogen-oxygen cell is a case in point, as it has been found to conform to the Helmholtz equation in spite of its irreversibility. The Helmholtz equation will apply to cells which are not strictly reversible, provided the irreversible process (in our case the oxidation of platinum) is accompanied by a relatively low heat of reaction.

Another application of the electromotive force method of investigating equilibria is the determination of transition points of allotropic modifications or of different salt hydrates. Investigations of this kind have been carried out by Cohen and others. A cell of the form

Zn	Saturated solution of $ZnSO_4 . 7H_2O$	Saturated solution of $ZnSO_4 . 6H_2O$	Zn

will give a current from left to right if the temperature is such that the hexahydrate tends to take up water and form the heptahydrate. The deposition of zinc at the hexahydrate electrode causes some of the solid hexahydrate to disappear, while a corresponding amount of solid heptahydrate is formed at the other electrode. At the transition temperature of the two hydrates (see p. 199), where they both have the same solubility, the E.M.F. of the cell must be zero. By varying the temperature it is usually possible to determine this point with great accuracy. This method can also be applied to salts of metals which cannot be used as reversible electrodes, such as sodium, by interposing so-called electrodes of the second kind. The transition point for

$$Na_2SO_4 . 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$$

was determined by Cohen in this way by means of the cell

$Hg . Hg_2SO_4$	$Na_2SO_4 . 10H_2O$ saturated	Na_2SO_4 saturated	$Hg_2SO_4 . Hg.$

Cohen's results for this cell are as follows: *

$t°$.	millivolts.	$t°$.	millivolts.	
28·3	36·6	32·7	−6·0	The transition
30·1	22·9	32·6	0	point is there-
32·0	6·4	—	—	fore 32·6°.
32·1	6·0	—	—	

Cohen determined the transition temperature for the white and gray modifications of tin by this method. He also investigated the variation with pressure of the transition temperature of the hydrates of zinc sulphate † by subjecting the galvanic cell to various pressures up to 1500 atm., and determining the vanishing point of the E.M.F. by varying the temperature at each pressure.

In this way he showed that the variation of the transition temperature with pressure is in close agreement with the thermodynamical formula (deduced in Chapter VII. p. 221) for the dependence of the melting point and the transition point on the temperature. For the differential coefficient $\frac{dT}{dp}$ he found

(*a*) from the E.M.F. determinations 0·0036°,

(*b*) from the heat of transition and the difference in volume between the two hydrates 0·0032°.

The only assumption made in the derivation of equation (2) (p. 347), apart from the two laws of thermodynamics, was the validity of the simple laws of solution. The equation is therefore also applicable to reactions which proceed practically to completion, so that the equilibrium cannot be investigated directly. This is the case in the great majority of galvanic cells, especially those which are used in practice, as it is only under these conditions that the equilibrium constant and therefore the E.M.F. can assume considerable values. It is, of course, impossible to predict the value of the E.M.F. in such cases (as K is unknown),

* *Zeitschr. f. physikal. Chemie*, **14**, 83 (1894); see also Cohen and Bredig, p. 535, *ibidem*.

† *Zeitschr. f. physikal. Chemie*, **75**, 1, 219 (1910).

but equation (2) tells us how E will vary with the concentrations of the substances used in making up the cell.

Thus, in the case of the Daniell cell discussed at the beginning of this chapter, we have the equation

$$E = \frac{RT}{2} ln\, K + \frac{RT}{2} ln \left[\frac{Cu^{\cdot\cdot}}{Zn^{\cdot\cdot}}\right],$$

where ($Cu^{\cdot\cdot}$) and ($Zn^{\cdot\cdot}$) are the ionic concentrations in the solutions and K is the equilibrium constant of the reaction

$$Cu^{\cdot\cdot} + Zn = Cu + Zn^{\cdot\cdot}.$$

The constant K cannot be determined analytically, as the precipitation of copper ions by zinc proceeds until practically all of the copper has been removed from the solution. We can calculate the value of K, however, from the E.M.F., E_0, of a Daniel cell in which the concentrations of the $Cu^{\cdot\cdot}$ and $Zn^{\cdot\cdot}$ ions are $1n$. Thus we have

$$E_0 = \frac{RT}{2} ln\, K = 1{\cdot}10 \text{ volt (at } 300^\circ \text{ abs.)}.$$

In order to calculate K, which has the dimensions (zero) of a pure number, we must express E_0 and R in the same system of units. In electrochemical units in which E_0 and R are expressed in volt coulombs, we have

$$E_0 = 1{\cdot}10 \times 96540 = 1{\cdot}062 \times 10^5,$$

$$R = 1{\cdot}985 \text{ cal.} = \frac{1{\cdot}985}{0{\cdot}24} = 8{\cdot}3 \text{ volt coulombs},$$

and hence

$$ln\, K = \frac{2 \times 1{\cdot}06 \times 10^5}{8{\cdot}3 \times 300} = 85{\cdot}3,$$

$$\log K = \frac{85{\cdot}3}{2{\cdot}3} = 37{\cdot}0,$$

and

$$K = 10^{37}.$$

The precipitation of $Cu^{\cdot\cdot}$ ions by metallic zinc will therefore proceed until the concentration of the $Zn^{\cdot\cdot}$ ions is 10^{37} as great as that of the $Cu^{\cdot\cdot}$ ions. The electromotive force of a Daniel cell of any concentration is given by the equation

$$E = E_0 + \frac{RT}{2} ln \frac{[Cu^{\cdot\cdot}]}{[Zn^{\cdot\cdot}]}.$$

From this equation it follows that addition of substances to the solutions in a galvanic cell can only affect its E.M.F., if they produce alterations in the concentrations of the substances taking part in the cell reaction. This is the case in a very marked degree when they form complex salts with the dissolved metallic salts. Thus the addition of cyanide of potassium to a Daniell cell diminishes its E.M.F., as the cyanide removes the copper ions from the solution to a much greater extent than the zinc ions. Under certain conditions this diminution may be so great as to reverse the sign of the E.M.F., namely, when the second term of the equation is more negative than the first is positive. Cells of this kind have been described by Hittorf. The addition of substances such as sodium chloride, sulphuric acid, and other substances which do not form complexes has no effect (in dilute solutions at least) on the E.M.F. of the cell.

Other cells made up in this way of two different metals, and also cells with inert electrodes whose E.M.F. depends on the presence of reacting gases (such as the hydrogen-oxygen cell), or of oxidising or reducing agents, and, finally, cells in which these various types are combined, may all be treated in a similar manner. In all cases it is necessary to obtain the chemical equation of the cell reaction, and to substitute the concentrations of the ions concerned in the logarithmic term.

3. Concentration cells.

The galvanic cells discussed hitherto (of the first kind) owe their power of yielding electrical energy to the forces of chemical affinity. A second type of cell makes use of the "dilution tendency" of dissolved substances (osmotic pressure). Galvanic cells of this type are called concentration cells. The thermodynamical theory of these cells was initiated by Helmholtz, and completed later on by Nernst.

Two cells of the first kind, connected in opposition to one another, and differing only in the concentrations of their respective solutions, constitute one type of concentration cell. As the E.M.F. of the two cells are not equal to one another, the combination is a cell of E.M.F. $\Delta E = E_1 - E_2$. The chemical changes which take place at the electrodes in one cell are exactly

reversed in the second. The only permanent change produced by the current is therefore a change in the concentration of the electrolytes. The thermodynamical calculation of the E.M.F. can be carried out for the case in which there is only a single electrolyte of variable concentration, *i.e.* when all but one of the electrolytes are present as saturated solutions in contact with solid.

As an example, let us consider two Clark cells

$$\mathrm{Hg} \;\Big|\; \begin{matrix}\text{Solution of } \mathrm{ZnSO_4} \\ \text{saturated with } \mathrm{Hg_2SO_4}\end{matrix} \;\Big|\; \mathrm{Zn}$$

with different zinc sulphate concentrations c_1 and c_2. When the first cell ($c_1 < c_2$) is in action, according to the equation $\mathrm{Zn} + \mathrm{Hg_2SO_4} = \mathrm{ZnSO_4} + 2\mathrm{Hg}$, solid zinc and solid mercurous sulphate disappear, and a corresponding amount of dissolved zinc sulphate and metallic mercury are formed. In the second cell, through which the same current passes in the opposite direction, an equal quantity of zinc sulphate and metallic mercury disappears, while zinc and solid mercurous sulphate are formed. The only permanent change in the system is therefore equivalent to the transference of zinc sulphate from one solution to the other. As such a transference would take place of its own accord only from a higher to a lower concentration, it follows from the laws of thermodynamics that work can only be obtained when the transference takes place in this direction. The cell with the lower concentration of zinc sulphate must therefore have the higher E.M.F.

We can calculate the E.M.F. ΔE of the combination, if we know the maximum work obtainable from the transference of 1 mol. of $\mathrm{ZnSO_4}$ from the concentrated to the dilute solution. (The work done against the atmospheric pressure owing to the change in volume of the solution may be neglected here.) It is sufficient for this purpose to calculate the work done when the transference is carried out reversibly. Helmholtz carried out this calculation for the isothermal distillation of the solvent from the dilute to the concentrated solution. Nernst calculated the osmotic work done in the process of dilution.

1. *Isothermal distillation.* Consider two cells differing in concentration by an indefinitely small amount dc. The

transference of 1 mol. of $ZnSO_4$ from the concentrated to the dilute solution, for which the electrical work done is $2dE$, is exactly reversed by the distillation from the concentrated to the dilute solution of the amount of water (n mols.) in which 1 mol. of $ZnSO_4$ of concentration c is dissolved. The work done in the distillation is $dw = nv\,dp = nRT\dfrac{dp}{p}$, where p is the vapour pressure of the solution and v the molecular volume of water vapour at temperature T and pressure p. We have therefore

$$dE = n\frac{RT}{2}\frac{dp}{p}.$$

The E.M.F. of a combination of two cells whose concentrations (c_1 and c_2) differ by a finite amount can be calculated by integrating this equation from n_1 to n_2, where n_1 and n_2 are the number of mols. of solvent in which 1 mol. of $ZnSO_4$ is dissolved in the two solutions of concentrations c_1 and c_2 respectively. In this way we obtain

$$\Delta E = E_1 - E_2 = -\frac{RT}{2}\int_{n_1}^{n_2} n\frac{dp}{p}$$

$$= -\frac{RT}{2}\left(n_2 \ln p_2 - n_1 \ln p_1 - \int_{n_1}^{n_2} \ln p\, dn\right). \quad \ldots..(3)$$

The integration can only be carried out when the vapour pressure p is known as a function of n or of the concentration c.

For dilute solutions Raoult's law may be applied, viz.

$$\frac{p_0 - p}{p_0} = \frac{1}{n+1} \quad \text{or} \quad p = p_0\frac{n}{n+1},$$

so that

$$n\frac{dp}{p} = \frac{dn}{n+1},$$

and

$$\Delta E = -\frac{RT}{2}\int_{n_1}^{n_2} n\frac{dp}{p} = -\frac{RT}{2}\ln\frac{n_2+1}{n_1+1} = \frac{RT}{2}\ln\frac{c_2}{c_1},$$

as n is large compared with 1 and $\dfrac{n_2}{n_1} = \dfrac{c_1}{c_2}$ in dilute solutions.

2. We arrive at the same result by calculating the maximum osmotic work done in the dilution. In diluting 1 mol. of $ZnSO_4$

from concentration c_2 to the smaller concentration c_1 by means of a semipermeable membrane, the amount of work done is $w = \int_{\pi_2}^{\pi_1} \pi \, dv$.

For dilute solutions we have, by van't Hoff's laws, $\pi = RTc$, and hence, since $c = \frac{1}{v}$,

$$w = -RT \int_{c_2}^{c_1} \frac{dc}{c} = RT \ln \frac{c_2}{c_1},$$

and therefore $\Delta E = \frac{w}{2} = \frac{RT}{2} \ln \frac{c_2}{c_1}$.

By similar reasoning we can calculate the influence of the concentration of acid on the E.M.F. of the lead accumulator. In this case the cell reaction may be represented by the equation

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O.$$

Two accumulators with different acid concentrations connected in opposition to one another give a current which results, so far as the solutions are concerned, in the apparent transference of 2 mols. of H_2SO_4 from the concentrated to the dilute cell, and of 2 mols. of water from the dilute to the concentrated cell.

As 2 mols. of H_2SO_4 and 2 mols. of water are transferred in opposite directions for each mol. of bivalent Pb, the work done per unit quantity of electricity is

$$\Delta E = w = RT \int_{n_2}^{n_1} (n-1) \frac{dp}{p}$$

$$= +RT \left(n_1 \ln p_1 - n_2 \ln p_2 + \ln \frac{p_2}{p_1} - \int_{n_2}^{n_1} \ln p \, dn \right).$$

This equation has been confirmed experimentally by Dolezaleck.*

4. Concentration cells with transference.

In the concentration cells which we have just been considering, the passage of the current produces concentration changes in two separate solutions.

There is another type of concentration cell, however, in which local changes in concentration are produced within a single

* *Theorie des Bleiakkumulators*, Halle, 1901.

solution. Cells of this kind are called concentration cells with transference. A cell of this kind consists of two electrodes of the same metal dipping into a solution of a salt of the metal, which has a different concentration at the two electrodes. When electricity flows through a cell of this kind, the current is divided between the anions and the cations according to their mobilities. For unit quantity of electricity $\nu = \frac{u}{u+v}$ equivalents of the cation, and $1-\nu = \frac{v}{u+v}$ equivalents of the anion traverse the cross-section of the cell, where ν is the transference number of the cation, and u and v are the ionic mobilities of the anion and cation.

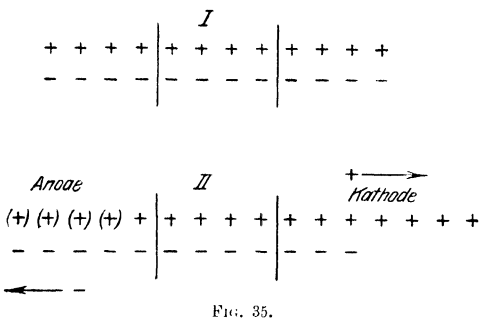


Fig. 35.

At the electrodes, however, one equivalent of the cation is deposited (or dissolved), since the amount deposited at the cathode, for example, is the sum of the amount ν carried by the current and the amount $1-\nu$ set free owing to the migration of the anions.

The concentration changes at the electrodes may be elucidated by the diagram (Fig. 35): I. represents the solution before the passage of the current, II. after the deposition of 4 cations. During the passage of the current 3 cations traverse the cross-section of the electrolyte in the positive direction of the current and 1 anion in the negative direction. In this example the transference number of the cation ν has been arbitrarily chosen as $\frac{3}{4}$ and that of the anion as $\frac{1}{4}$.

At the anode the 4 free anions are neutralised by the dissolution of metal from the electrode (indicated by the crosses in brackets).

As may be seen from the figure, the solution at the anode (to the left) has become more concentrated, and the solution at the cathode (to the right of the vertical lines) has become poorer in electrolyte, while the concentration of the middle portion is unchanged. The increase in the quantity of electrolyte at the anode is $4 \times \frac{1}{4}$, and the decrease at the cathode is also 1 equivalent, so that the total number of equivalents of electrolyte in the solution is unchanged. The passage of the current results therefore in the transference of $1-\nu=\frac{1}{4}$ equivalents of the electrolyte from the cathode to the anode for each equivalent of metal deposited.

If the cell: metal | concentrated solution | dilute solution | metal is capable of yielding a current, the direction of the current must be such that the concentrated solution becomes more dilute and the dilute solution more concentrated. The positive current must therefore flow from the dilute to the concentrated solution inside the cell, so that the electrode dipping into the concentrated solution becomes the cathode. As $1-\nu$ equivalents of the electrolyte $=2(1-\nu)$ equivalents of the ions are transferred by unit quantity of electricity from the more concentrated (cathode) solution to the more dilute (anode) solution, the E.M.F. of this concentration cell can be calculated by the same two methods (p. 354) which Helmholtz and Nernst employed in the calculation of the E.M.F. of concentration cells without transference. Thus, for dilute solutions of an n-valent metallic salt, we have the equation

$$E=\frac{2RT}{n}(1-\nu)\,ln\,\frac{c_2}{c_1}=\frac{RT}{n}\cdot\frac{2v}{u+v}\cdot ln\,\frac{c_2}{c_1}. \quad \ldots\ldots\ldots\ldots(4)$$

Reversible metallic electrodes immersed in solutions of varying concentrations of their salts are termed electrodes of the first kind. Reversible electrodes of the second kind are metallic electrodes immersed in a saturated solution of a sparingly soluble salt, whose solubility is determined by the concentration of a soluble salt with the same anion. Metallic silver immersed in KCl solution saturated with AgCl is an electrode of the second kind. The concentration of the $Ag^{\cdot}$ ions in the solution is determined by the concentration of the Cl' ions, *i.e.* of the KCl. In a galvanic cell made up of two such electrodes, the current

is carried almost entirely by the ions of the soluble salt ($K^{\cdot}$ and Cl'), which are present in large excess. During the passage of unit quantity of electricity, ν equivalents of the cation $K^{\cdot}$ are carried in the positive direction of the current to the cathode, and $1-\nu$ equivalents of the anion Cl' to the anode. The electrical neutrality of the solution is preserved by the interaction of the $\nu+1-\nu$ $K^{\cdot}$ ions set free at the cathode with 1 equivalent of solid AgCl, according to the equation

$$K^{\cdot}+AgCl=KCl+Ag^{\cdot}$$

and the subsequent neutralisation and precipitation of the $Ag^{\cdot}$ ions as metallic silver. The concentration of the electrolyte increases at the cathode by the amount ν corresponding to the migration of the cations, since the anions necessary are supplied from the solid phase. The electrode behaves therefore as if it were capable of supplying anions to the electrolyte during the passage of the current. Electrodes of the second kind, which act in this way, are described as reversible for the anion.

The reverse process takes place at the anode in a cell of this type. Thus $1-\nu$ equivalents of the anion migrate to the anode, where they react with the metal of the electrode to form the insoluble salt, leaving the concentration of the electrolyte unaltered.

The concentration of the solution at the anode is therefore diminished by ν owing to the migration of ν equivalents of the cation towards the cathode. The effect of the passage of the current is to transfer ν equivalents of the soluble electrolyte from the anode to the cathode.

Thus, if two electrodes of the same metal are immersed in differently concentrated solutions of a salt which has the same anion as the sparingly soluble salt of the electrode metal with which the solution is saturated, the current produced by the cell will be in the direction which produces a dilution of the more concentrated solution. The metal dipping into the concentrated solution will therefore be the anode inside the cell.

The electrode (anode) which is immersed in the concentrated solution is dissolved during the passage of the current.

The E.M.F. of a cell made up of two reversible electrodes

of the second kind in solutions of unequal concentrations is therefore given by

$$E = \frac{RT}{n} 2\nu \ln \frac{c_2}{c_1} = \frac{RT}{n} \frac{2u}{u+v} \ln \frac{c_2}{c_1}.$$

In the equation for the E.M.F. of a cell with electrodes reversible for the cation, the transference number of the anion appears as a factor, and *vice versa*.

In the experimental application of these equations, we must remember that c refers to the ionic concentration and not to the total concentration. We cannot therefore expect our equations to be in exact agreement with experiment as long as we are ignorant of the exact value of the degree of ionisation. Conversely, however, we may use an experimental determination of the E.M.F. to calculate the degree of ionisation or the transference number. The validity of the Nernst equations has been placed beyond doubt by the results of numerous measurements.

Nernst showed also that the E.M.F. of a concentration cell with transference such as

$$\mathrm{Ag} \;\Big|^{1}\; \underset{c_1}{\mathrm{AgNO_3}} \;\Big|^{2}\; \underset{c_2}{\mathrm{AgNO_3}} \;\Big|^{3}\; \mathrm{Ag}$$

is made up of three discontinuities of potential at the three boundaries numbered 1-3. By calculating the osmotic work which the electrical forces must do in carrying the ions across the boundaries, Nernst obtained the equations

$$\begin{aligned} \epsilon_1 &= \frac{RT}{n} \ln \frac{c_1}{C}, \\ \epsilon_2 &= \frac{RT}{n} \ln \frac{v-u}{u+v} \ln \frac{c_1}{c_2}, * \qquad \text{.....(5)} \\ \epsilon_3 &= \frac{RT}{n} \ln \frac{C}{c_2}, \end{aligned}$$

and hence

$$E = \epsilon_1 + \epsilon_2 + \epsilon_3 = \frac{RT}{n} \frac{2v}{u+v} \ln \frac{c_1}{c_2} = \frac{RT}{n} 2(1-\nu) \ln \frac{c_1}{c_2},$$

which is identical with equation (4) except for the sign.

* The dilute solution ($c_1 < c_2$) becomes positively charged at the surface of contact when $u > v$.

C is a constant which is characteristic of the metal of which the electrode is composed, and is sometimes called the electrolytic solution pressure. Its numerical value is equal to the ionic concentration of a solution against which the metal would have no difference of potential. This quantity is of the greatest importance for the electrochemical behaviour of the metal. It cannot be determined, however, by measurement with concentration cells, for the solution pressure C disappears from the sum of the various potential differences in equation (5). The calculation of C from the total E.M.F. would be possible if we could choose the ionic concentration of one solution, say c_2, so that the potential difference ϵ_3 would be zero. Numerous experiments have actually been carried out with the object of constructing an electrode which would have the "absolute potential" zero against the solution. These experiments, although in themselves interesting and important, are based on special electrochemical hypotheses and not on purely thermodynamical principles. They are therefore beyond the scope of this book.*

Although it is not yet possible to determine with certainty the absolute value of the potential difference between a metal and a solution, we can determine its value relative to an arbitrarily fixed standard of potential difference by determining the E.M.F. of the cell

Metal | solution | standard electrode.

The standard electrodes most commonly used are the hydrogen electrode (platinum immersed in 1n H_2SO_4 solution under hydrogen at atmospheric pressure) and the calomel electrode (mercury against 1n KCl saturated with HgCl). The potential differences at the surface of contact between the two liquids may either be eliminated by the addition of suitable intermediate solutions † or estimated by calculation from the known values of the concentrations and mobilities of the various ions present.‡ In this

* Ostwald, *Zeitschr. f. physikal. Chemie*, **1**, 583 (1887); Billiter, *Zeitschr. f. Elektrochemie*, **8**, 638 (1902); *Zeitschr. f. physikal. Chemie*, **48**, 513 (1904); Palmaer, *Zeitschr. f. physikal. Chemie*, **59**, 129 (1907).

† See Bjerrum, *Zeitschr. f. physikal. Chemie*, **53**, 428 (1905); *Zeitschr. f. Electrochemie*, **17**, 58 (1911).

‡ Planck, *Wiedem. Ann.* **40**, 561 (1890); Nernst, *ibidem*, **45**, 360 (1892); Henderson, *Zeitschr. f. physikal. Chemie*, **59**, 118 (1907); **63**, 325 (1908).

way we can compare the potential differences between various metals and the solutions of their salts (at the same ionic concentration), and arrange them in a series of relative "normal potentials" (ionic concentration = 1). The results are given in the following table, in which the potential of the hydrogen electrode (as defined above) is taken as zero:*

Metal.	ϵ.	Metal.	ϵ.
Zn	−0·76 volt.	H_2	+0·00 volt.
Fe	−0·43 ,,	Cu	+0·34 ,,
Cd	−0·40 ,,	Ag	+0·80 ,,
Ni	−0·22 ,,	Hg	+0·86 ,,
Pb	−0·12 ,,	Au	+1·5 ,,
Sn	−0·10 ,,		

This sequence of the metals, arranged according to their solution pressures, corresponds exactly to the Voltaic sequence, in which each metal becomes positively charged when brought into contact with the preceding metal of the sequence. The correspondence between these two sequences is at once intelligible if we assume that there is always a thin layer of liquid which acts as an electrolyte between the two metals in contact, so that each pair of metals may be regarded as a small galvanic cell. Whether or not the voltaic series would remain unaltered if the metals were immersed in non-aqueous solutions of their salts is a question which cannot be decided by thermodynamical reasoning. So far the experimental evidence seems to show that the series is at least approximately the same in water as in other solvents.†

* *Potentialsammlung der Deutschen Bunsen-Gesellschaft*, Halle, 1911. See also G. N. Lewis, *Journ. Amer. Chem. Soc.* **vol. xxxv.** 1 (1913).

† See Sackur, *Zeitschr. f. Electrochemie*, **11**, 385 (1905); Abegg u. Neustadt, *Zeitschr. f. physikal. Chemie*, **69**, 486 (1909).

CHAPTER XI.

THERMOELECTRICAL PHENOMENA.

1. Joule's law and the electrical equivalent of heat.

Joule's law states that an electric current produces in a circuit an amount of heat which is proportional to the square of the current intensity, to the resistance in the circuit, and to the duration of the current. The heat produced in the circuit is therefore given by

$$Q = kI^2\omega t.$$

If Q is measured in calories, I in amperes, ω in ohms, and t in seconds, the constant k is called the electrical equivalent of heat. According to the latest and most accurate measurements the value of this constant is 0·2392,* so that a current of 1 ampere produces in a resistance of 1 ohm approximately 0·24 calorie per second. This production of heat is entirely irreversible. No current is produced when the circuit is heated from the outside.

Joule's law is strictly accurate so long as the conductor in which the evolution of heat is measured is homogeneous and at a uniform temperature throughout. If these conditions are not complied with, deviations from the law are obtained, and the evolution of heat is found to be no longer completely irreversible. By raising the temperature of certain parts of the circuit, electric currents can now be obtained. These reversible phenomena are called thermoelectrical phenomena in the more restricted sense of the term. In common with all other reversible processes, they must follow certain regularities, which are deter-

* *Phys. Rev.* **34**, 180 (1911). See also G. N. Lewis, *Journ. Amer. Chem. Soc.* **35**, 4 (1913).

mined by the second law of thermodynamics. These will be briefly discussed in the following.

2. The Thomson effect.

W. Thomson (Lord Kelvin) observed that the electric current is accompanied by an apparent transference of heat when the temperature in the circuit is not uniform. Thus heat is either absorbed or produced (according to the nature of the conductor) wherever the temperature is not uniform along the conductor. This effect is reversed by reversing the direction of the current. If a current in one direction produces a cooling effect at a given part of the circuit, a current in the opposite direction will produce a heating effect at the same place. Substances in which the apparent transference of heat is in the same direction as the (positive) current were called by Lord Kelvin positive substances (*e.g.* copper) and the others negative. If the fall in temperature along a wire (in the direction of the current) is $t°$, a current of intensity i will produce per second the amount of heat σti. The constant σ depends on the nature of the metal, and was called by Thomson the specific heat of electricity. The following table gives the values of σ as a function of the temperature for a variety of metals:*

Fe $\sigma = -[1{\cdot}860 + 0{\cdot}02057t - 0{\cdot}00005120t^2] \times 10^{-6}$ cal. per amp.

Cu $\sigma = +[3{\cdot}01 + 0{\cdot}00662t] \times 10^{-7}$ - - - ,, ,,

Ag $\sigma = +[7{\cdot}363 + 0{\cdot}00887t] \times 10^{-7}$ - - - ,, ,,

Constantan

$\sigma = -[4{\cdot}73 + 6{\cdot}10 \times 10^{-3}t - 2{\cdot}40 \times 10^{-5}t^2] \times 10^{-6}$,, ,,

The numerical value of σ always increases with the temperature, but is not always proportional to the absolute temperature, as some authors have stated.

Conversely, we must assume that wherever we have a fall of temperature along a wire, we must also have a fall of potential. It is, however, impossible to detect this fall of potential when the circuit is composed of one metal only, as the sum of the potential differences round the whole circuit is zero. If the

* Lecher, *Ann. d. Physik* (4), **19**, 853; **20**, 480, 1906.

potential difference between parts of the wire differing in temperature by dT is $dE=f(T)dT$, the total potential difference

$$E=\int_T^T f(T)dT=0.$$

If the circuit is made up of different metals, the phenomena are complicated by the processes which take place at the boundaries between the various conductors. We shall therefore discuss these first.

3. Peltier effect.

When a current flows through the boundary between two different metals, heat is either absorbed or set free at the boundary according to the nature of the pair of metals. This phenomenon is called the Peltier effect, after its discoverer.

When the current is reversed, the sign of the heat evolution is also reversed. The heat evolved is again proportional to the temperature and to the duration of the current. We shall write $+q$ for the heat evolved by 1 ampere in 1 second. q is a function of the temperature and of the nature of the two metals.

The Peltier effect has been shown to be reversible, and is therefore subject to Le Chatelier's principle, like all reversible processes. Thus, when the boundary between two metals is heated, an electromotive force must be produced. The direction of this E.M.F. must be such as to oppose a current which would produce a positive Peltier effect (that is, a heating effect) at the boundary. Thus a current will flow in a closed circuit made up of two different metals when the two boundaries are at different temperatures. No current will flow when the two boundaries are at the same temperature, even when the temperature at other parts of the circuit is not uniform. In the first case the E.M.F. in the circuit is $E=E_1-E_2+E_1'-E_2'$, where E_1 and E_2 are the potential differences at the two boundaries at the temperatures T_1 and T_2, and E_1' and E_2' are the potential differences corresponding to the Thomson effects in the two metals. The value of E is not altered by the interposition of another conductor (*e.g.* a galvanometer) between the two metals, provided the surfaces of contact between this intermediate conductor and the two metals of the thermocouple are kept at the same temperature T_1.

According to the pioneering experiments of Seebeck, who discovered the thermoelectric potentials in 1823, we may arrange the metals in a series such that each metal becomes positively charged at the hot join with respect to the preceding metal of the series. The same summation law holds for the thermoelectric potential difference between any two metals as in the voltaic sequence, namely that it is equal to the sum of the potential differences between the intermediate members of the series. Thus, in the series A, B, C, D, etc., the potential difference AD between A and D is equal at the same temperature to $AB+BC+CD$. The thermoelectric series is approximately as follows :

$-$ Na, K, Bi, Ni, Co, Pd, Hg, Pt, Au, Cu, Sn, Al, Pb, Zn, Ag, Cd, Fe, Sb, $+$

Different observers do not always agree as to the exact order of the metals in the series, as the value of the thermoelectric potential difference is affected in a marked degree by the temperature and the purity of the metal.

The potential difference E at the surface of contact between two metals is a function of the temperature $E=f(T)$.

The Thomson effect is small in comparison with the Peltier effect, and may be neglected to a first approximation. The thermoelectric current is therefore determined by the potential difference $E_1-E_2=f(T_1)-f(T_2)$. In the simplest case we may assume that E is a linear function of the temperature, so that $E=E_0+aT$. We have then

$$E_1-E_2=a(T_1-T_2),$$

i.e. the thermoelectric force is proportional to the difference in temperature between the hot and cold joins. This simple case, however, applies only to a few pairs of metals, and even then only for a limited range of temperature. A somewhat more general assumption is

$$E=E_0+aT+bT^2.$$

We have then

$$\begin{aligned} E_1-E_2 &= a(T_1-T_2)+b(T_1^2-T_2^2) \\ &= (T_1-T_2)[a+b(T_1+T_2)]. \end{aligned}$$

This equation was found to apply to a large number of couples by Avenarius in 1863. Experiment has shown that b may be either positive or negative.

In the latter case $E_1 - E_2$ passes through a maximum as the temperature is raised, namely, where $T_1 = -\frac{a}{2b}$ (T_2 being constant and $< T_1$).

In this case each value of $E_1 - E_2$ corresponds to two different values of $T_1 - T_2$. The relation between these two quantities is then no longer unique. A couple with a negative value of b is thus useless for measuring temperature (see p. 13). The thermoelectric E.M.F. vanishes when $T_1 + T_2 = -\frac{a}{b}$.

The following tables give the values of the Peltier effect and the thermoelectric E.M.F. of various metals for a temperature difference of 1 degree:

1. Peltier Effect.*

A current capable of depositing 1·314 gr. Cu (4000 coulombs) produces at the junction between Cu and

Pure	Sb	− 14·5 cal.
Commercial	Sb	− 5·4 ,,
,,	Fe	− 2·8 ,,
,,	Cd	− 0·51 ,,
,,	Zn	− 0·43 ,,
German silver		+ 2·75 ,,
Pure	Bi	+ 21·3 ,,

2. Thermoelectric Potential of Various Metals.

(*a*) Determined by Noll † between 0° and 1° C. The positive current goes from the 2nd to the 1st metal at the hot junction.

Ni—Cu	$21{\cdot}9 \times 10^{-6}$ volt.	Cu—Hg	$6{\cdot}0 \times 10^{-6}$ volt.
Co—Hg	$12{\cdot}4 \times 10^{-6}$,,	Au—Hg	$6{\cdot}0 \times 10^{-6}$,,
Fe—Cu	$10{\cdot}5 \times 10^{-6}$,,	Ag—Hg	$5{\cdot}5 \times 10^{-6}$,,

Sn—Cu	$3{\cdot}8 \times 10^{-6}$ volt.
Pb—Cu	$2{\cdot}8 \times 10^{-6}$,,
Mg—Cu	$2{\cdot}9 \times 10^{-6}$,,

* Le Roux, *Ann. de Chim. et de Phys.* (4), **10**, 201 (1867).

† *Wiedem. Ann.* **53**, 874 (1894).

(*b*) Determined by Holborn and Day * between 0° and $t°$ in millivolts for platinum.

t.	Au.	Ag.	Rh.	Ir.	Pd.	90 Pd 10 Ru	90 Pt 10 Pd	10 Pt 90 Pd
+950	15·532	17·484	12·798	11·688	10·670	9·814	4·068	2·566
+450	5·270	5·320	4·422	4·146	3·296	4 102	1·714	−0·290
−80	−0·307	−0·302	−0·302	−0 320	−0·392	−0·388	−0·087	+0·146
−185	−0·130	−0·160	−0·160	−0·283	−0·774	−0·534	−0·106	+0·240

(*c*) Determined by Jaeger and Diesselhorst † for Pt against each of the following metals in millivolts between 0° and 100°. (The positive sign signifies that the positive current passes from platinum to the other metal at the hot junction.)

Au	+0·72	Ni	−1·62
Ag	+0·71	Fe	+1·45
Cu	+0·72	Pb	+0·41
Pd	−0·56	Constantan (60 % Cu, 40 % Ni)	−3·44
Zn	+0·75		
Sn	+0·42	Manganin (84 % Cu, 2 % Ni, 12 % Mn)	+0·57
Al	+0·38		
Cd	+0·85	Bi	−0·62

The couple generally used at low and moderate temperatures, viz. Fe/constantan, has therefore a thermoelectric E.M.F. of $+1·45+3·44=4·9$ millivolts.

4. Thermodynamic relationships between thermoelectric E.M.F., Thomson effect, and Peltier effect.

Since electrical energy can be converted at will into mechanical energy, a thermoelectric current is capable of doing work at the expense of the heat which is supplied from the outside to the circuit at the hot junction ($E_1>E_2$). In his classical thermodynamical theory W. Thomson assumed that the thermoelectrical phenomena were strictly reversible, except for the production of "Joule heat," which becomes negligible as the current strength approaches zero. In this limiting case, therefore, the heat produced or absorbed at the junctions is equal

* *Verhandl. d. Deutsch. physikal. Gesellschaft* (1899), 691.

† *Abhandl. d. physikal.-techn. Reichsanstalt*, **3**, 269 (1900).

to the Peltier effect which an equal current in the opposite direction would produce at these junctions.

Let the circuit (Fig. 36) consist of two metals 1 and 2 in contact with one another at the junctions A and B. Let the temperature of A be $dT°$ higher than that of B. If dE is the potential difference in the circuit, the passage of unit quantity of electricity will produce the electrical energy dE. At the same time an amount of heat dq will be absorbed by the system at A, and a smaller amount of heat $q-dq$ will be given out at B. In addition the heat $\sigma_1 dT$ due to the Thomson effect will be produced in the wire 1 and the heat $\sigma_2 dT$ in the wire 2.

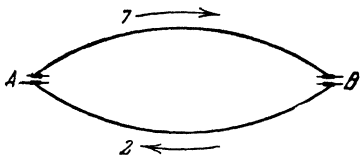


FIG. 36.

By the first law the electrical energy produced is equal to the heat absorbed less the heat given out, *i.e.*

$$dE = dq + (\sigma_2 - \sigma_1)dT. \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

By the second law the ratio of the amount of heat transformed into work to the total heat absorbed by the system is equal to the ratio of the difference in temperature to the temperature of the hot junction.

Hence
$$\frac{dE}{q+\sigma_2 dT} = \frac{dT}{T}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Neglecting $\sigma_2 dT$ in comparison with the finite amount of heat q, we obtain

$$q = T\frac{dE}{dT}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Differentiating (3) and substituting in (1), we obtain

$$\sigma_2 - \sigma_1 = -T\frac{d^2E}{dT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The Peltier effect q is therefore determined by the first derivative, and the difference of the Thomson effects by the second derivative of the thermoelectric E.M.F.

Comparing (3) and (4) with the Helmholtz equation for the E.M.F. of a galvanic cell, we find that the Peltier effect corresponds to the latent heat of the cell and the values of σ (the

specific heats of electricity) to the specific heats of the cell materials.

Equation (3) was first confirmed experimentally by Jahn.* The temperature at which the thermoelectric E.M.F. is a maximum for a given couple is of special interest. At this point, called the inversion point, $\frac{dE}{dt}$ and q are both zero, so that the Peltier effect vanishes.

P. Cermak † has shown that equation (4) is sometimes not very well confirmed by experiment. The quantities of heat produced by the Peltier and Thomson effects are, however, very small, and the calorimetrical determinations are not nearly so accurate as the measurements of the thermoelectric E.M.F. by the compensation method, especially as the quantities of heat to be determined are differences between actual calorimetrical determinations and the Joule heats calculated from electrical data. We are therefore not yet in a position to condemn the fundamental assumptions of Thomson's theory. As the thermodynamical equations are rigorously accurate, any error in the conclusions must be sought for in the assumption of the complete reversibility of the phenomena.

It is possible to test Thomson's equations in another way. According to the experiments of Battelli,‡ the Thomson effect is proportional to the absolute temperature for a large number of metals, *i.e.*

$$\sigma = aT. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Hence $$\sigma_2 - \sigma_1 = (a_2 - a_1)T = -T\frac{d^2E}{dT^2},$$

from which it follows that the thermoelectric potential is a quadratic function of the difference in temperature between the hot and cold junctions, as required by the formula of Avenarius (p. 366). Deviations from this formula must therefore be due to deviations from equation (5).

5. Other theories of thermoelectricity.

As in most other branches of physics and chemistry, numerous attempts have been made to supplement the thermo-

* *Wiedem. Ann.* **34**, 755 (1888).

† *Jahrb. d. Radioaktivität und Elektronik*, **8**, 241 (1911).

‡ *Nuovo Cim.* (3), **21**, 228, 250; **22**, 157, 221 (1887).

dynamical theory of the thermoelectrical phenomena by kinetic theories. These attempts have indubitably brought us nearer to an understanding of the phenomena. We shall refrain from discussing these theories * in detail here. The more recent of them are all based on the electron theory of metallic conduction. They assume that the free electrons are held with different degrees of firmness by the atoms of the various metals, and that their dissociation from the metal is influenced by the temperature in a manner which varies from metal to metal. Krüger compares this tendency of the electrons to escape from the metal to the vapour pressure of a liquid, and uses the thermodynamical formulae which apply to the evaporation of liquids, in calculating the dissociation of the electrons. He has succeeded in calculating the potential differences between

metal/vacuum and metal 1/metal 2

by the Nernst equations for galvanic cells. In this way he is able to deduce not only Thomson's equations, but also the voltaic series, which cannot be obtained by pure thermodynamics.

The thermoelectrical behaviour of many alloys is typical. Their thermoelectric potential is often much higher than that of the pure metals of which they are composed. These facts cannot be deduced from thermodynamics, which in general can tell us nothing new about constants which are characteristic of the chemical nature of substances. We must have recourse here to special theories, just as in the calculation of the osmotic pressure of solutions. We may mention that the electronic and molecular theories of R. Schenck † and A. Bernoulli ‡ have done valuable service in this direction.

* The literature is given by Cermak, *loc. cit.*; see also Krüger, *Physikal. Zeitschr.* **11**, 800; **12**, 360; and K. Baedeker, *ibid.* **11**, 809.

† *Ann. d. Physik* (4), **32**, 261 (1910).

‡ *Ann. d. Physik* (4), **33**, 690; *Verhandl. d. Deutsch. physikal. Gesellsch.* **13**, 213 (1911).

CHAPTER XII.

THERMODYNAMICS AND CAPILLARITY.

1. Fundamental definitions.

Small quantities of liquids invariably tend to assume the spherical shape. In other words, they tend to assume the form in which the surface for a given volume is as small as possible. The surface of a liquid therefore behaves as if it were an elastic skin, which tends to contract as much as possible. In order to increase the surface in any manner,

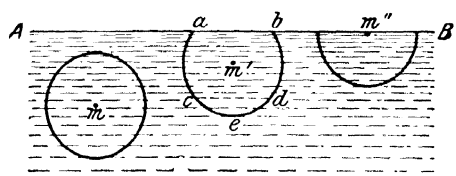


FIG. 37*a*.

a certain amount of work must be done. To explain these facts Laplace assumed that neighbouring particles of the liquid exert an attraction on one another (in contradistinction to the molecules of a gas). In the interior of the liquid these forces neutralise one another, as their action is uniform in all directions. At the surface, however, there will be a resultant force towards the interior, the magnitude of which will depend on the form of the surface. This will become clear from a consideration of Fig. 37*a* and *b*. As the range through which the forces act is assumed to be small, the forces will neutralise one another at a point in the liquid, provided the sphere described about the point, with radius equal to the range of the forces, is entirely within the liquid. If the point is near the surface, however,

the forces within the space *abcd* alone neutralise one another, while the forces due to the portion *cde* exert a tension on the surface towards the interior of the liquid. It is apparent from

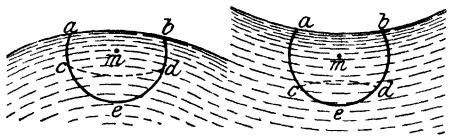


FIG. 37*b*.

the figure that this tension is greater at a concave than at a convex surface. According to Laplace, the force attracting unit surface towards the interior is $= K \pm \frac{H}{R}$. At constant temperature K and H are constants for each liquid, *i.e.* they are independent of the shape of the surface. R is the radius of curvature of the surface. The positive sign applies to convex, the negative to concave surfaces. The force per unit area of a plane surface ($R = \infty$) is equal to K, and is called the internal pressure of the liquid.

Thus all liquids tend to assume a form in which the total force attracting the surface towards the interior is a minimum. This is the case when the surface itself is a minimum; in other words, when the liquid has assumed the spherical shape. Every departure from the spherical shape involves an increase in the surface, and therefore necessitates the doing of work, as particles of the liquid have to be brought from the interior to the surface against a force acting towards the interior. It is easy to show * that the work done in increasing the surface of the liquid by da at constant temperature is equal to $\frac{H}{2} . da$. It is therefore proportional to the increment of area. The quantity $\frac{H}{2} = \gamma$ is called the *surface tension* of the liquid. It has the dimensions energy/surface or force/distance (dyn./cm.). The quantity H, as we have just stated, is independent of the shape and magnitude of the surface, so that the surface tension is independent of the apparent stretching of the surface. Surface tension is therefore essentially different from the stress produced by

* The proof will be found in any of the larger text-books on physics. See also Freundlich, *Capillarchemie*, 1909.

stretching an elastic membrane, with which we compared it at the beginning of this paragraph.

By surface energy is generally meant the product of the surface of a liquid and its surface tension. It is therefore dependent on the magnitude of the surface and on the nature of the liquid. The surface energy is a minimum for a given mass of liquid when the shape of the liquid is spherical. Any increase in the surface of the liquid involves the doing of work by external forces, and increases the surface energy.

2. Isothermal and adiabatic increase of surface.

The above definition of surface energy is misleading, as the energy supplied from the outside in order to increase the surface of the liquid at constant temperature is not completely converted into surface energy, but is partly used up in compensating a cooling effect, which would appear if the surface were increased adiabatically. The total energy supplied is therefore the sum of two terms $\gamma\, da + q\, da$, of which the first, *i.e.* the "surface energy," alone can be entirely converted into mechanical work. It would therefore be more correct to define the quantity γa as the "free surface energy" in accordance with Chapter VI. p. 173.

We can prove by means of the second law that an isothermal increase in the surface (by unit area) must be accompanied by an absorption of heat (q). With this end in view, let us consider the following cycle. By the expenditure of the amount of work $\gamma\, da$, let the surface be increased by da at the temperature T. Let the heat absorbed in this process be $q\, da$. Now cool the liquid by dT and allow the surface to return isothermally to its original dimensions. As both γ and q must in general be regarded as functions of the temperature, the work $(\gamma - d\gamma)da$ will be regained and the heat $(q - dq)da$ evolved in this process. Now raise the temperature of the liquid by dT, thus completing the cycle. The work done by the system in this reversible cycle is $-d\gamma\, da$. The heat absorbed at the higher temperature T is $q\, da$, and the heat given out at the lower temperature is $(q - dq)da$. Hence, by the second law,

$$\frac{dw}{Q} = -\frac{d\gamma\, da}{q\, da} = \frac{dT}{T} \quad \text{or} \quad q = -T\frac{d\gamma}{dT} \qquad \ldots\ldots\ldots\ldots(1)$$

Experiment has shown that $\frac{d\gamma}{dT}$ is negative for all liquids, so that the surface tension diminishes as the temperature is raised. At the critical point we know that the surface tension must be zero, since the liquid and its vapour are identical at that temperature. Thus q is always positive, so that heat is always absorbed during an isothermal increase in surface, and the temperature always falls when the surface is increased adiabatically.

For many liquids the surface tension is a linear function of the temperature, provided the critical point is not approached too closely. We have then $\frac{d\gamma}{dT} = -\text{const.}$, and the total energy necessary to produce unit surface is $\Gamma = \gamma + q = \text{const.}$, that is, independent of the temperature. This relationship, however, is not valid in the neighbourhood of the critical point, at which both γ and q become zero.

The total energy of unit area of the surface is $\gamma + q$. γ, on the other hand, is the free energy of the surface which can be completely converted into mechanical work (see p. 373). Using the notation of Chapter VI. p. 186, we have $U = \gamma + q$ and $\psi = \gamma$. Thus, from the Helmholtz equation,

$$\psi = U + T\frac{\partial \psi}{\partial T},$$

we obtain $$\gamma = \gamma + q + T\frac{\partial \gamma}{\partial T} \quad \text{or} \quad q = -T\frac{\partial \gamma}{\partial T},$$

in agreement with the result obtained above by means of a reversible cycle (equation (1)).

3. Vapour pressure of small drops.

These thermodynamical considerations are due in the main to Lord Kelvin. He also was the first to recognise the fact that the vapour pressure of a liquid is dependent on the magnitude and shape of the surface. Let us calculate the work dw which can be obtained by allowing the mass dm of a liquid whose surface tension is γ, and whose density is s, to evaporate from a sphere of radius r to a plane surface. The mass m of the sphere is $\frac{4}{3}\pi r^3 s$ and its surface a is $4\pi r^2$. When the mass of the small sphere of liquid is diminished

by dm, its surface is diminished by da, and we gain the amount of work $\gamma\, da$. If we take the mass dm of the liquid from the small sphere and add it to a large mass of the same liquid, whose surface is a plane (*i.e.* a sphere of infinite radius), the area of the plane surface will not be altered appreciably. The work done in the addition of the small amount dm to the large sphere is therefore zero. We can calculate the total work done, $dw = \gamma\, da$, with the aid of the following equations:

$$m = \tfrac{4}{3}\pi r^3 s, \qquad a = 4\pi r^2,$$
$$dm = 4\pi r^2 s\, dr, \qquad da = 8\pi r\, dr$$
$$= \frac{2}{rs}\, dm.$$

Hence
$$dw = \frac{2\gamma}{rs}\, dm.$$

The same amount of work may be obtained reversibly in a different manner, viz. by the isothermal distillation of the amount dm from the small sphere to the plane surface. Let p be the ordinary vapour pressure of the liquid at the plane surface and p' its vapour pressure at the small sphere. If the vapour obeys the gas laws, the work done in the transference is

$$dw = \frac{RT}{M}\, ln\, \frac{p'}{p}\, dm,$$

where M is the molecular weight of the vapour.

From this it follows that

$$ln\, \frac{p'}{p} = \frac{2\gamma}{rs}\, \frac{M}{RT} > 0. \qquad \text{.....(2)}$$

The vapour pressure at a convex surface is therefore greater than the vapour pressure at a plane surface. In a similar way it may be shown that the vapour pressure at a concave surface is less than at a plane surface.

As a first approximation we may write

$$ln\, \frac{p'}{p} = \frac{p' - p}{p},$$

and therefore
$$p' = p\left(1 + \frac{2\gamma}{rs}\, \frac{M}{RT}\right). \qquad \text{.....(3)}$$

The alteration in the vapour pressure is, however, very small. For water at the ordinary temperature ($T = 300$) the difference

is only 1 per cent. for $r = 10^{-5}$.* For practical purposes we may therefore generally neglect the difference $p' - p$, although it is sufficient to account for the instability of small drops in presence of large drops. The increased vapour pressure of small drops also accounts for the fact that supersaturated vapours condense preferably on small dust particles and other nuclei.

4. Melting point and surface tension.

Similar considerations apply to the surface tension of solids. Although surface tension between solids and gases has never been accurately measured, there can be no doubt of its

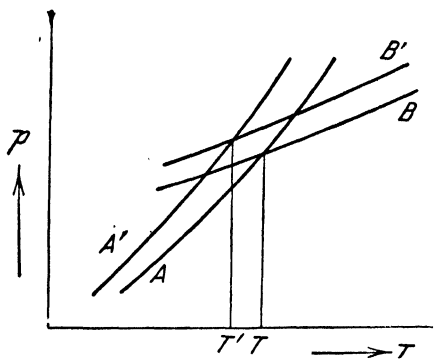


FIG. 38.

existence.† Otherwise it would be difficult to explain the fact that large solid particles tend to grow at the expense of smaller particles, and that very small crystals have a greater solubility than larger crystals. It is probable, indeed, that the surface tension between solids and gases is greater than between liquids and gases. The experiments of Pawlow ‡ on the melting point of small particles of salol are in favour of this view. The melting point (see p. 231) is the temperature at which the vapour pressure of the solid and liquid phases are equal. In the accompanying figure, A and B represent the vapour pressure curves of ordinary solid

* $\gamma = 75$ dyne/cm., $r = 10^{-5}$, $M = 18$,
$R = 0{\cdot}8 \times 10^8$, $s = 1$, $T = 300$, $\frac{2\gamma \cdot M}{rsRT} = 0{\cdot}01$.

† See Freundlich, *l.c.* p. 89. ‡ *Zeitschr. f. physikal. Chemie*, **74**, 562 (1910).

and liquid salol. A' and B' are the corresponding curves for a very small particle of solid or drop of liquid. (The volume of both is assumed to be the same as a first approximation.) The melting point of the small particle is T'. T' might be either greater or less than T according as the distance between A and A' is greater or less than the distance between B and B'. Pawlow found that the melting point of salol is lowered by diminishing the size of the particles. A' is therefore further from A than B' from B. As the vapour pressure differences are determined by the surface tension (*ceteris paribus*) according to the above formula, it would appear that the surface tension of the solid is greater than that of the liquid.*

5. Surface tension of solutions.

The surface tension of a liquid is altered when a substance is dissolved in it. This follows at once from Laplace's conception of capillarity, as the attraction between neighbouring particles of the liquid must be dependent on the number and on the nature of the dissolved particles. We are also led to conclude that the distribution of the solvent and solute molecules in space is not necessarily the same at the surface as in the interior, since the force of attraction acting on a solvent molecule at the surface is not necessarily the same as that on a molecule of the solute. We should therefore expect to find a difference in concentration between the solution at the surface and in the interior. We cannot decide *a priori* whether the concentration of the solute in the surface layer will be greater or less than in the interior, as this must depend on the nature of the two components of the solution. On the other hand, we can show by purely thermodynamical methods that there must be a relationship between the concentration at the surface and the surface tension. W. Gibbs was the first to draw attention to this fact. The second part of the following derivation is similar to that given by Freundlich (*loc. cit.*). The demonstrations given by the earlier writers are, however, less simple than that given below.

* Küster (*Lehrbuch d. physikal. Chemie*, p. 189) overlooks the fact that the liquid phase also appears, in the first instance, in the form of small drops.

Work is done when any solution is diluted in a reversible manner. Let v be the volume and π the osmotic pressure of the solution. The maximum work done when the solution is diluted isothermally by dv is $\pi\,dv$. If we now allow for the fact that the surface of the solution is increased by da during the dilution (which we may suppose to be performed by isothermal distillation from a large volume of the solvent), we must subtract the work $\gamma\,da$ due to the surface tension. Hence the free energy of the solution diminishes during dilution by

$$-d\psi=\gamma\,da-\pi\,dv.$$

Since $d\psi$ is a complete differential, by the second law, it follows that

$$\left(\frac{\partial\gamma}{\partial v}\right)_a=-\left(\frac{\partial\pi}{\partial a}\right)_v. \quad \text{.....(4)}$$

This equation states that the osmotic pressure of a solution will be diminished by increasing its surface at constant volume, provided that the surface tension is increased by an increase in dilution at constant surface, and *vice versa*. The meaning of equation (4) becomes plainer when the concentration c is substituted for the volume v of the solution. Let the total number of molecules in the volume v of the solution be n, and let the excess at the surface be u per unit area. In calculating the concentration c in the interior of the solution, the total number of molecules n must be diminished by ua, so that we obtain

$$c=\frac{n-ua}{v},$$

and hence

$$\frac{\partial c}{\partial u}=-\frac{u}{v},\quad \frac{\partial c}{\partial v}=-\frac{n-ua}{v^2}.$$

Substituting in (4), we obtain

$$-\frac{\partial\gamma}{\partial c}\frac{n-ua}{v^2}=\frac{\partial\pi}{\partial c}\frac{u}{v}$$

or

$$u=-c\frac{\dfrac{\partial\gamma}{\partial c}}{\dfrac{\partial\pi}{\partial c}}. \quad \text{.....(5)}$$

As $\dfrac{\partial\pi}{\partial c}$ is positive for all solutions, u and $\dfrac{\partial\gamma}{\partial c}$ are always opposite in sign. The surface tension of a solution will therefore increase

with concentration, if the surface has a smaller concentration than the interior, and *vice versa.*

In dilute solutions we may apply van't Hoff's law $\pi = RT \cdot c$. Substituting this in equation (5), we obtain

$$u = -\frac{c}{RT} \cdot \frac{\partial \gamma}{\partial c}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Equations (5) and (6) have been confirmed qualitatively by several investigators. A summary of the literature will be found in Freundlich's book. The equations have recently been tested in a quantitative manner by W. C. M'C. Lewis.* He investigated the surfaces between two non-miscible liquids, such as mercury and an aqueous solution, to which the same relationships apply. In some cases he obtained an entire confirmation of equation (6). In other cases, particularly when electrolytes were present, he found deviations, which he was able to explain, however, as being due to electrocapillarity.

Equations (5) and (6) are probably the key to all adsorption phenomena, as Freundlich points out.

A further remarkable consequence of equation (5) concerning the form of the surface tension-concentration curve for mixtures of two liquids was discussed by Gibbs. A small quantity of a dissolved substance may produce a marked diminution in the surface tension, but can never increase it to any great extent.

If there is a diminution $\left(\frac{\partial \gamma}{\partial c} < 0\right)$, the solute will be absorbed at the surface, and the relative excess in concentration $\frac{u}{c}$ can attain to considerable values, in consequence of which the $\gamma - c$ curve may fall off very rapidly. On the other hand, if there is an increase in surface tension, the surface will always contain less solute than the dilute solution. The quotient $\frac{u}{c}$ must therefore always be small, so that the $\gamma - c$ curve must be only slightly curved. For such pairs of liquids we should expect to find a curve of the form shown in Fig. 39. Curves of this kind have

* W. C. M'C. Lewis, *Phil. Mag.* (6), **15**, 499 (1908); **17**, 466 (1909); *Zeitschr. f. physikal. Chemie*, **73**, 129 (1910).

been observed repeatedly. Thus Drucker * gives the following figures (plotted in Fig. 39) for mixtures of water and butyric acid.

The addition of electrolytes to water generally produces a slight rise in surface tension, while the addition of organic substances generally produces a marked diminution.

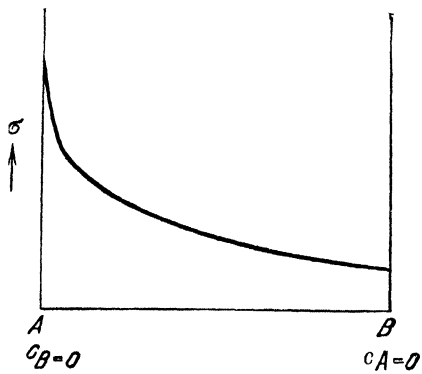


FIG. 39.

c mols. butyric acid per litre.	$\sigma_{25°}$.
0	74·2
0·01583	72·9
0·08247	62·6
0·2675	49·8
0·4353	43·6
0·9802	34·5
2·834	29·4
9·015	28·3
11·38	27·3
(pure acid)	

The laws of thermodynamics thus give us a relationship between the increase or decrease in concentration at the surface layer, and the change in surface tension with the concentration. They tell us nothing about the absolute values of these quantities, however, nor about their relationship to the chemical or physical characteristics of the substances concerned. The experiments of van der Waals, Bakker, and others on this subject will not be discussed here, as they have not yet been brought to an entirely satisfactory conclusion. The further development of this subject is of very great importance, however, and the significance of capillarity in numerous physical, chemical, and biological questions is now universally recognised.

* *Zeitschr. f. physikal. Chemie*, **52**, 641 (1905).

CHAPTER XIII.

HEAT RADIATION.

1. Fundamental definitions.

We have stated already, in the earlier part of this book, that heat can be propagated by radiation as well as by conduction. By radiation we mean any effect which progresses in all directions of space in straight lines with a very great velocity, and which, in contradistinction to conduction, does not require a material medium for its propagation, but, on the contrary, is always weakened in passing through matter. It is customary to distinguish between material radiation (cathode and canal rays, α and β radium rays) and energy radiation (light, heat, and electrical radiation). We shall restrict ourselves in the following to the latter, and in particular to that part of the theory which depends on the laws of thermodynamics.

As there is no impediment to the propagation of radiation through empty space, we are only able to detect its presence by observing the changes which the radiation produces in material bodies on which it falls. By the energy of the radiation is meant, in accordance with the first law, the maximum value of the sum of all the different kinds of energy which the radiation can produce in a body on which it falls. By the intensity of the radiation is meant the amount of energy which falls per second on unit area perpendicular to the direction of propagation. The emissivity of a body is the amount of energy radiated per second from unit area of its surface. Radiation can originate only in material bodies.

When radiant energy falls on a material body it is divided

into three parts. One part is reflected (according to the laws of reflection at a smooth surface, and diffusely at a rough surface). Of the remainder which penetrates into the body, part is absorbed in the body, *i.e.* is transformed into some other form of energy (chemical, electrical, heat energy, etc.), and the rest is transmitted through the body and appears again at the other side. The fraction R of the total energy which is reflected at the surface is called the reflectivity, the fraction A which is absorbed is called the absorptivity, and the remaining fraction T the transmissivity of the body, so that for all bodies $R+A+T=1$. Radiant energy, as theory and experiment have shown, is not uniform in character, but may be regarded as being composed of a large number of different kinds of energy which have all the same velocity of propagation, but which differ from one another in wave length or vibration number. At every point

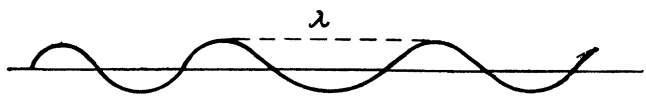


FIG. 40.

of a space through which radiation is passing, the intensity of the radiation is periodic in character. If we were able to make an instantaneous picture of a space transmitting homogeneous radiant energy, and then to plot the intensity of the radiation as ordinate at each point in the direction of propagation, we should obtain a wave curve of the kind shown in Fig. 40. (In reality the curve would be more complicated in character, but Fig. 40 may be taken as typical of the kind of curve which we should obtain.) The distance between two points at which the state of vibration is the same is called the wave length λ. The number of vibrations per second at each point is called the vibration number ν. These two quantities are connected with one another by the equation $\lambda\nu=c$. c is the velocity of propagation of the radiation. In vacuo this velocity has been found to be 3×10^{10} cm. per second.

The total radiation may be regarded as composed of a large number of rays of different wave length and vibration number, but all having the same velocity. The energy of the radiation

corresponding to wave lengths between the limits λ and $\lambda+d\lambda$ is denoted by the symbol U_λ. The total energy of the radiation is therefore $U=\int_0^\infty U_\lambda d\lambda$. As this sum is finite, U_λ must vanish at the two limits 0 and ∞. As we shall show more fully in the following, the value of U_λ for any given value of U must pass through at least one maximum. In the case of what is called complete radiation (see § 3 below), the curve of U_λ against λ is of the type shown in Fig. 41. The energy of the radiation is thus concentrated about a definite wave length.*

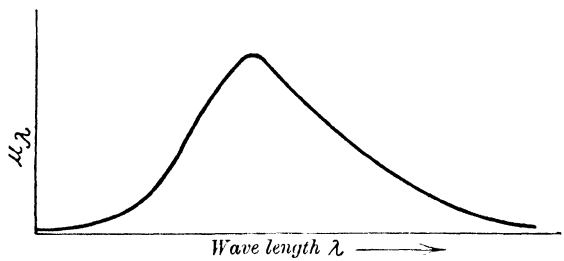


FIG. 41.

When the radiant energy U falls on a material body, the reflected, absorbed, and transmitted portions can each be resolved into a sum over the various wave lengths. Thus, for example,

$$AU=\int_0^\infty (AU)_\lambda d\lambda=\int_0^\infty A_\lambda U_\lambda d\lambda.$$

In general the absorptivity, reflectivity, and transmissivity are functions of the wave length, and the energy of each wave length is resolved independently of the others into these three portions.

2. The laws of Kirchhoff.

The only kind of radiation which we shall consider in the following is that which is produced by heat energy, and which on absorption is entirely reconverted into heat energy, and we shall therefore exclude chemical and electrical phenomena both as cause and as effect of the radiation. Radiation of this kind is

* A comparison is suggested here with the molecules of a gas, which can likewise have any value between 0 and ∞, but which are grouped preferentially about the "most probable" velocity.

called pure temperature radiation in contradistinction to luminescence phenomena, such as those observed in Geissler tubes and in certain chemical reactions. Temperature radiation is subject to certain important laws, the discovery of which is mainly due to Kirchhoff.

Consider a number of bodies of any shape and composition enclosed in an otherwise empty chamber whose walls are impermeable to heat. In course of time an equilibrium will be established in which, by the laws of thermodynamics, the bodies must all be at the same temperature. This equilibrium is, however, not a statical but a dynamical equilibrium, in which each body is radiating outwards (emitting) as much heat as it is absorbing from the external radiation. Let E be the emissivity of one of the bodies, S the area of its surface, K the intensity of the radiation falling on its surface, and A its absorptivity. We have then

$$\text{emitted energy} = \text{absorbed energy},$$

or
$$ES = AKS, \text{ and hence } \frac{E}{A} = K. \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Equation (1) applies to all bodies in thermal equilibrium with one another. K depends solely on the state of the radiation in the intervening space, and is therefore independent of the specific properties of the body. While the emissivity E and the absorptivity A may vary from body to body, their ratio at constant temperature is always the same.

The physical significance of the constant K may be obtained from the following consideration. A body which absorbs all the radiation which falls on it, and which therefore neither reflects nor transmits even the smallest fraction of it, has the absorptivity $A = 1$, and is called a perfect black body. (Charcoal is a very close approximation to a perfect black body.) For a perfect black body, equation (1) assumes the form

$$E_B = K,$$

and hence for a body which is not black

$$\frac{E}{A} = E_B. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1a)$$

As A is always a proper fraction, this equation states that the emissivity of any body is always less than the emissivity of a perfect black body at the same temperature, and further that the lower the absorptivity of a body the lower is its emissivity.

It follows also that the intensity of the radiation inside a closed chamber in temperature equilibrium is the same as that emitted by a perfect black body at the same temperature, no matter whether the chamber contains a black body or not. (In future a chamber of this kind will be termed a "Prevost chamber," after the French physicist Prevost, who first made use of it in physical reasoning.)

These laws apply not only to the radiation as a whole, but also to the radiation corresponding to each wave length individually. Thus, if E, E_B, and A can be written as sums (or integrals) of the form $E = \int_0^\infty E_\lambda \, d\lambda$, etc., where the summands (or integrands) are independent of one another, we have for each wave length

$$\frac{E_\lambda}{A_\lambda} = E_{B_\lambda}.$$

E_λ and A_λ are functions of the chemical properties of the body and of the wave length, but their ratio at constant temperature is solely a function of the wave length, and is equal to the emissivity of a black body for the same wave length. The black body has therefore the greatest emissivity of all bodies for all wave lengths.

Kirchhoff's applications of these laws to the spectrum of the sun are well known. A body emitting temperature radiation absorbs all the wave lengths which it emits, and *vice versa*. A sodium flame, for example, must absorb light of all the wave lengths which are emitted by another sodium flame. (Inversion of the Na-line.) In this way Kirchhoff arrived at his exceedingly fruitful theory of the Fraunhofer lines in the spectrum of the sun.

If a body is transparent for any colour, it is incapable of emitting this colour. If a body has a high absorptivity for any colour, its emissivity for that colour will approach that of the black body for the same colour.

These laws apply, however, only to bodies in vacuo or in the same homogeneous medium. The emissivity of two black bodies in two different media A and B of refractive index n_a and n_b are in the ratio

$$E_{B_a} : E_{B_b} = n_a^2 : n_b^2.$$

3. The laws of radiation for a perfect black body.

As radiation is propagated through space with a finite velocity, there must be a certain amount of energy in each unit of volume of a space through which radiation is passing. This amount of energy is called the energy density u. The energy in a space of volume V is then $U = uV$. In a closed space in thermal equilibrium the radiation is the same as that emitted by a black body. The state of the radiation and its energy density would therefore be unaltered by the introduction of an indefinite number of black bodies at the same temperature. The energy density of the radiation in the closed space is independent of the total volume, and is solely a function of the temperature $u = f(T)$. The form of the function $f(T)$ may be derived as follows.

Consider a Prevost chamber of volume V (whose walls are impermeable to heat). Let its temperature be T and the energy density of the radiation in its interior be u. Let the chamber be furnished with a movable and frictionless piston (also impermeable to heat) which separates the interior of the chamber from the external (empty) space.

Let us now push forward the piston so as to diminish the volume of the chamber from V' to V. If it were possible to perform this operation without doing work, the total energy of the chamber would be the same as before, but the energy density of the radiation would have increased, since

$$uV = u'V'.$$

We have therefore $u' > u$, and hence $T' > T$. Thus we should have raised the temperature of the chamber without doing work and without altering its internal energy. This is incompatible with the second law of thermodynamics, and we conclude therefore that our original assumption must be false, *i.e.* that it is impossible to displace the piston without doing work. The radiant energy in the Prevost chamber must therefore exert a

pressure on the piston similar to the pressure of a gas. The necessity for the existence of such a pressure was demonstrated thermodynamically by Bartoli in 1876. Still earlier Maxwell had shown it to be a consequence of his electromagnetic theory of radiation. Recently this pressure has been actually measured by Lebedew and by Nichols and Hull.*

The magnitude of this pressure cannot be calculated by thermodynamical methods. From Maxwell's electromagnetic theory of radiation, however, it follows that the pressure p exerted by radiation (force per unit area) is given by

$$p = \tfrac{1}{3}u. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

This is in accord with the experimental determinations of Lebedew and of Nichols and Hull.

We are now in a position to deduce the equation of state of a Prevost chamber, and to determine the change in the energy density of the radiation produced by an adiabatic change in volume. The work done in compressing the radiation by dV is $p\,dV = \frac{u}{3}dV$. If the compression is performed adiabatically, this amount of work is entirely used up in increasing the energy uV of the radiation. Hence we obtain

$$-\frac{u}{3}dV = d(uV) = u\,dV + V\,du,\dagger$$

and therefore

$$\tfrac{1}{3}u\,dV + v\,du = 0.$$

Integrating this, we obtain

$$u^{\frac{4}{3}}V = \text{const.} \qquad (3)$$

The equation for the radiation pressure $p = \frac{u}{3}$ also enables us to determine the function $u = f(T)$ by means of the second law of thermodynamics. The amount of work $-p\,dV = -\frac{u}{3}dV$ is the increase in the free energy $d\psi$ produced by an isothermal change in the volume of the Prevost chamber. The total energy

* The literature on the pressure of radiation is summarised by F. Hasenöhrl, *Jahrb. d. Radioaktivität u. Elektronik*, 2, 267 (1905).

† The left-hand side is negative because the energy increases when V is diminished.

U is equal to uV, and hence, from the Helmholtz equation $\psi = U + T\frac{d\psi}{dT}$, it follows that

$$-\frac{u}{3}V = uV - \frac{T}{3}\frac{du}{dT}V,$$

or
$$4u\,dT = T\,du,$$

and hence
$$u = \text{const. } T^4. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The emissivity of a black body is therefore given by the equation
$$E_B = \sigma T^4. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4a)$$

Thus the energy density of the radiation in a Prevost chamber and the emissivity of a perfect black body are both proportional to the fourth power of the absolute temperature. The constant σ is of universal significance, and applies to all black bodies of whatever materials they may be composed.

Equation (4) is known as the law of Stefan and Boltzmann. Stefan arrived at this law in an empirical manner from the rough experimental material then at his disposal. Boltzmann gave the above thermodynamical proof involving Maxwell's expression for the radiation pressure.

Many years later the law was accurately established experimentally by the work of Lummer in conjunction with Wien, Pringsheim, and Kurlbaum, in a series of researches begun in 1895.

These investigators were able to realise a practically perfect black body by making use of the theorem proved above, that the radiation in a Prevost chamber at constant temperature is "black." The radiation emitted from a small opening in the walls of the chamber is the same as that emitted by a black body. They found the value of the constant σ to be $1{\cdot}28 \times 10^{-12}$ cal. This is the amount of energy emitted per second from a square centimetre of a black body at the temperature 1° absolute into a space at 0° abs.

The law of Stefan and Boltzmann is exactly valid for an absolutely black body in vacuo, as it is based on the two laws of thermodynamics and on Maxwell's equations of the electromagnetic field, which are exact under these conditions. The law of Stefan and Boltzmann may therefore be used not only

to measure temperature, but also to define the absolute scale of temperature. The perfect black body has therefore the same significance in theory as the perfect gas. We can calculate the work done in a reversible cycle between two black bodies at different temperatures by the law of Stefan and Boltzmann, and arrive in this way at the same analytical formulation of the second law as that obtained in Chapter V. by means of the equation of state of a perfect gas.* A perfect black body can no more be realised in nature than a perfect gas. Both are limiting conceptions, to which experiment can, no doubt, approximate very closely, but can never absolutely attain. For practical temperature measurements the gas thermometer can be used at best only up to 1600°, as no material has yet been found which is impermeable to gases above this temperature. The radiation from a black body is the only means of measuring higher temperatures than this in the absolute thermodynamic scale.

Combining equations (3) and (4), we obtain

$$T^3V = \text{const.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4b)$$

Thus, for an adiabatic change in volume, the temperature of a Prevost chamber is inversely proportional to the cube root of the temperature.

4. The displacement law of Wien.

The law of Stefan and Boltzmann gives us a relationship between the total energy of black radiation (also called complete, or full, radiation) and the temperature. It tells us nothing, however, about the relative magnitudes of the contributions from different parts of the spectrum (wave lengths) to the total energy. In other words, it tells us nothing about the way in which the total energy is distributed over the various monochromatic radiations, nor how the distribution varies with the temperature.

This distribution law cannot be deduced by purely thermodynamical methods. A great step forward, however, was made by W. Wien, who showed that the wave length of maximum

* See Cl. Schaefer, *Archiv. f. Mathematik u. Physik* (3), **12**, 34.

energy becomes shorter as the temperature is raised. Wien's considerations are partly thermodynamical and partly based on the wave theory of radiation.

When a ray of light is reflected from a moving mirror, its wave length is altered in accordance with Doppler's principle. Thus, if the mirror (A) is moving in the direction of the normal (AB) to its surface, a ray of wave length λ will be converted by reflection into a ray of wave length

$$\lambda' = \lambda\left(1 - \frac{2v\cos\theta}{c}\right),$$

where θ is the angle between the incident ray and the normal, and c is the velocity of light. The wave length is therefore unaltered by reflection from a stationary mirror ($v = 0$) or by reflection at grazing incidence ($\cos\theta = 0$) from a moving mirror.

This uniform monochromatic radiation enclosed in a chamber with perfectly reflecting walls will remain monochromatic as long as the walls remain stationary. As soon as we begin to compress the radiation, however, by moving forward one of the walls, the wave lengths of all rays which are reflected from the wall while it is in motion will be altered in accordance with the above equation. After compression, therefore, the radiation will no longer be monochromatic, but part of it will have been converted into radiation of shorter wave lengths. If instead of monochromatic radiation we had taken "black body" or complete radiation, the wave lengths of all the constituent monochromatic radiations of which it is composed would have been shortened in a similar manner. The distribution of the total energy over the various wave lengths is therefore altered by an adiabatic compression. Calculating the effect of an adiabatic compression on the distribution by means of Doppler's principle, Wien was able to show that the emissivity E_λ of a black body for the wave length λ must be given by the equation

$$E_\lambda = \frac{c^2}{\lambda^5} F\left(\frac{\lambda T}{c}\right),^* \qquad \text{.....(5)}$$

where T is the temperature and c is the velocity of light.

* The derivation of this equation is somewhat lengthy, and need not be discussed here. An excellent treatment of Wien's law will be found in Planck's *Vorl. über d. Theorie der Wärmestrahlung*, 2nd ed. p. 68 *et seq.*

The form of the function F cannot be determined in this way. Equation (5) is the most general form of Wien's displacement law.

Since E_λ is zero for $\lambda = \infty$ and for $\lambda = 0$, it follows that there must be a value of λ for which E_λ is a maximum. At the maximum we have

$$\frac{dE_\lambda}{d\lambda} = 0,$$

or

$$-\frac{5}{\lambda^6} F\left(\frac{\lambda T}{c}\right) + \frac{1}{\lambda^5}\frac{T}{c}\frac{d}{d\left(\frac{\lambda T}{c}\right)}\left\{F\left(\frac{\lambda T}{c}\right)\right\} = 0,$$

which may also be written

$$\frac{\lambda T}{c}\dot{F}\left(\frac{\lambda T}{c}\right) - 5F\left(\frac{\lambda T}{c}\right) = 0, \quad \text{.....(6)}$$

where $\dot{F}$ is the differential coefficient of F with respect to $\frac{\lambda T}{c}$.

Equation (6) determines a definite value of $\frac{\lambda T}{c}$, so that we obtain

$$\lambda_m T = \text{const.} = b, \quad \text{.....(7)}$$

where λ_m is the wave length at which E_λ is a maximum.

Thus the wave length of maximum emissivity is displaced in inverse proportion to the absolute temperature. This is in accord with the fact that the radiation emitted by a black body does not become visible until relatively high temperatures, and that its colour goes from red to yellow to white as the temperature is raised.

Combining equations (5) and (7), we obtain

$$E_{\lambda_m} = \frac{c^2 T^5}{b^5} F\left(\frac{b}{c}\right) = \text{const. } T^5. \quad \text{.....(5)}$$

The maximum emissivity is therefore proportional to the fifth power of the temperature.

The table on p. 392 shows the agreement between Wien's displacement law and the experimental results of Lummer and Pringsheim.*

Even at a bright-red heat the maximum emissivity is still far in the ultra-red invisible part of the spectrum. It does not

* *Verhandl. d. Deutsch. physikal. Gesellschaft*, 2, 163 (1900). Deviations from the law were found at greater wave lengths however.

reach the visible region of the spectrum until about 4000° C. The maximum emissivity in the spectrum of the sun is at about $0{\cdot}5\mu$. If the sun were a perfect black body, this would mean that its temperature must be about 5800° C.

T.	$\lambda_{max.}$	$\lambda_{max.}\,T$.
836·5	3·5 μ	2928
1087	2·61 „	2837
1377	2·10 „	2892
1416	2·02 „	2860
	Mean	2879

5. The distribution of energy in the spectrum.

The final problem of the theory of radiation is the determination of the emissivity of a black body for any wave length as a function of the wave length and the temperature; in other words, the determination of the form of the function $F\left(\frac{\lambda T}{c}\right)$ in equation (5). The complete solution of this problem is beyond the scope of pure thermodynamics, even when supplemented by the ordinary wave theory of radiation.

Indeed, the complete distribution law for all wave lengths and temperatures has not yet been established on a thoroughly sound theoretical basis. For large values of λT, *i.e.* for large wave lengths and high temperatures, a satisfactory formula has, however, been obtained. This formula was first discovered by Lord Rayleigh, and has been deduced in several different ways by Jeans, H. A. Lorentz, and M. Planck. It would lead us too far afield to attempt to enter into a full discussion of this question here, but the following derivation of Rayleigh's law will suffice to show the general lines on which a solution of this important problem may be obtained.

It is universally agreed nowadays that radiation is electromagnetic in character. When an electrically charged particle is subjected to rapid accelerations it produces electromagnetic disturbances in the surrounding space. The nature of these disturbances can be calculated by Maxwell's theory of the electro-

magnetic field, and many of the properties of radiation can be satisfactorily accounted for by the assumption that radiation is due to such electromagnetic disturbances. Thus the emission of spectrum lines and the selective absorption of flames emitting spectrum lines may be ascribed to the existence of oscillators within the atoms of the vapour. By an oscillator (the term is due to Planck) is meant a system capable of executing electrical vibrations. An electron, or small charged particle, bound by forces to a centre of equilibrium within an atom, is an example of an oscillator. When an oscillator is exposed to electromagnetic radiation, it is under the influence of rapidly alternating electrical forces, and will therefore execute vibrations. It can be shown that an oscillator will respond most readily to radiation of its own frequency, much as a sound resonator responds most readily to sound waves of its own pitch. When an oscillator has been exposed for a sufficient length of time to uniform radiation, it will reach a steady state in which the energy which it absorbs per second from the radiation is exactly equal to the energy which it emits per second. Planck showed that the mean energy U of an oscillator is related to the intensity E_λ of the radiation of wave length λ in the complete radiation with which it is in equilibrium by the equation

$$U = \frac{3\lambda^4 E_\lambda}{c}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Here λ is the wave length emitted by the oscillator and c is the velocity of light. The mean energy of the oscillator is therefore proportional to the intensity of that part of the complete radiation which has the wave length emitted by the oscillator itself.

The energy of the oscillator can, however, be calculated from the kinetic theory in much the same way as we calculated the energy of a monatomic gas. The mean kinetic energy of the oscillator can be shown to be equal to the mean kinetic energy of an atom of a monatomic gas at the same temperature. The oscillator has, however, a certain amount of potential energy in virtue of the forces which bind it to its centre of equilibrium. The mean potential energy of the oscillator can be shown to be equal to its mean kinetic energy, so that the total energy of the

oscillator (kinetic plus potential) must be just twice that of a gas atom at the same temperature. We have therefore

$$U = \frac{3RT}{N}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

where R is the gas constant and N the number of atoms in a gram atom. Combining equations (9) and (10), we obtain

$$E_\lambda = \frac{cRT}{N\lambda^4} = \frac{CT}{\lambda^4}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

This is Rayleigh's radiation law. It is a consequence of the ordinary laws of electrodynamics and statistical mechanics. Nevertheless, it is certainly erroneous. For long waves and high temperatures, equation (11) is approximately in accord with experiment, and the agreement becomes better as the wave length is increased. The shorter the wave length, however, the greater the discrepancy between Rayleigh's law and the experimental facts becomes. For infinitely short waves it is clear that Rayleigh's law cannot be true, for by equation (11) we have $E_\lambda = \infty$ for $\lambda = 0$, whereas the emissivity of an actual black body falls off rapidly to zero towards the ultra-violet end of the spectrum. The reason for this discrepancy has not yet been clearly elucidated.

For short waves and high temperatures an empirical equation due to W. Wien has been found to represent the facts remarkably well. It is

$$E_\lambda = \frac{k_1}{\lambda} e^{-\frac{k_2}{\lambda T}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

It is possible to obtain a mathematical derivation for this equation in various ways by introducing certain new assumptions, but none of the theories yet put forward are thoroughly satisfactory. Wien's law must therefore still be regarded as largely empirical. It is as much at fault in the region of long wave lengths as Rayleigh's law in the region of short wave lengths.

The failure of Rayleigh's law may be ascribed either to an error in the statistical calculation, or to the inapplicability of the ordinary laws of mechanics to very rapid vibrations. Adopt-

ing the latter point of view, Planck assumed that the energy of an oscillator does not vary continuously, but by finite increments or "quanta" of energy, each having the same value $\epsilon = h\nu = \frac{hc}{\lambda}$ for an oscillator of frequency ν. In this way he obtains the equation

$$E_\lambda = \frac{c^2 h}{\lambda^5} \frac{1}{e^{\frac{chN}{R\lambda T}} - 1} = \frac{c_1}{\lambda^5} \frac{1}{e^{\frac{c_2}{\lambda T}} - 1}. \quad \text{.....(13)}$$

For infinitely long waves $\epsilon = \frac{hc}{\lambda}$ becomes infinitely small, so that the energy of the oscillator varies continuously, as in the classical theory. In this case Planck's law degenerates into Rayleigh's law, as may easily be seen by approximating for $\lambda = \infty$ in equation (13). For short waves, equation (13) approximates to

$$E_\lambda = \frac{c^2 h}{\lambda^5} e^{-\frac{chN}{R\lambda T}}, \quad \text{.....(14)}$$

which is identical with Wien's law (12) if we put $c^2 h = k_1$ and $\frac{chN}{R} = k_2$.

Planck's law represents the experimental facts better than any other law which has yet been proposed, and is probably accurate to within the experimental errors. The "quantum" hypothesis has also proved very fruitful in other branches of physics. The question of the distribution law cannot, however, even yet be regarded as definitely settled.

6. The optical measurement of temperature.

The laws of radiation enable us to measure temperature in four different ways, viz.

(1) Determination of the intensity of the total radiation and calculation of the temperature by the law of Stefan and Boltzmann,

$$E = \sigma T^4.$$

(2) Determination of the wave length of maximum intensity and calculation of the temperature by Wien's law,

$$\lambda_{\max.} \cdot T = A.$$

(3) Determination of the maximum intensity,

$$E_{\max.} = B \,.\, T^5.$$

(4) Determination of the intensity for any given wave length and calculation of the temperature by Planck's distribution law,

$$E_\lambda = \frac{c_1}{\lambda^5} \frac{1}{e^{\frac{c_2}{\lambda T}} - 1}.$$

Methods (1), (2), and (3) involve measurements in the ultra-red by means of the bolometer. Method (4) can be carried out by means of a spectrophotometer. A very convenient form of optical pyrometer, based on this method, is that of Wanner. A definite part of the spectrum (generally in the red) is isolated from the light emitted by the body whose temperature is to be measured, and its intensity is compared with the intensity of the same wave lengths in the spectrum of a nearly perfect black body (generally a carbon filament lamp through which a constant current is passed). The intensities of the two rays are made equal by rotating an analysing Nichol in the path of the unknown ray (previously polarised) until it appears equally bright in the field of view with the ray from the carbon filament. Holborn and Kurlbaum dispense with the Nichols, and regulate the current in the filament until the two sources of light appear equally bright. In practice, Wanner's method seems to be the better of the two.

The practical application of the optical method of measuring temperature is made possible by the fact that the radiation from most solid bodies at high temperatures corresponds very closely to that from a perfect black body. In many metallurgical processes the temperature of a mass of material in a furnace has to be measured, and here the blackness of the radiation is still more perfect, as the furnace acts to a certain extent like a Prevost chamber.

In calculating the temperature for a constant wave length, Wanner used Wien's radiation law in the form

$$\log E = a - \frac{b}{T}.$$

For small values of λT, namely up to about $\lambda T = 3000$, this equation gives values almost identical with those calculated from Planck's law. This condition is fulfilled for visible wave lengths at not too high temperatures.

Lummer and Pringsheim determined the temperature of a black body by methods (1), (3), and (4), and obtained the following very concordant values :

By (1) (on the average) 2335° abs.,
,, (3) ,, ,, 2325° ,,
,, (4) ,, ,, 2320° ,,

CHAPTER XIV.

THE NERNST HEAT THEOREM.

1. Relationship between affinity and heat of reaction according to the two laws of thermodynamics.

In Chapter IX. it was shown that the affinity of a chemical reaction can be calculated for any temperature, provided its value is known (from experiment) for any one temperature, and provided the heat of reaction and the variation of the heat of reaction with the temperature are known for the range of temperature in which we wish to calculate the affinity. The heat of reaction and its temperature coefficient, which is determined by the specific heats of the reacting substances, can both be determined calorimetrically without difficulty. On the other hand, it is not possible to calculate the affinity or the position of a chemical equilibrium by means of the two laws of thermodynamics and these thermal quantities alone. It is always necessary to know in addition the value of the affinity for some one temperature. The experimental determination of the affinity is often attended with considerable difficulty. It was therefore eminently desirable to discover a new method which would avoid even this single determination and enable us to calculate the affinity from thermal quantities alone. The valuable researches of Nernst which resulted in the discovery of his "heat theorem" have placed at our disposal a means of solving this important problem.*

In order to show the connection between the new theorem and the laws of thermodynamics, let us return for a moment

* *Göttinger Nachrichten*, 1906; see also Nernst, *Theoretische Chemie*, 6th edition, p. 699.

to the relationship between the affinity and the heat of reaction which we derived from the two laws of thermodynamics alone. The heat of reaction Q_p and the affinity A for any reaction are both functions of the temperature, say $Q_p = f(T)$ and $A = \phi(T)$. The form of these functions is not known in general, and may vary from case to case. The first differential coefficients of these functions have, however, a definite physical significance, and therefore give us some information as to the properties of the functions themselves. Thus $\frac{dQ_p}{dT} = f'(T) = -\Sigma c_p$ is the sum of the specific heats of the reacting substances, where the terms in the sum corresponding to the substances which are formed with evolution of heat are taken positive. Similarly,

$$\frac{dA}{dT} = \phi'(T) = -\Sigma S$$

is the sum of the entropies of the reacting substances. These two sums are both functions of the temperature, and vary continuously throughout a range of temperature in which the reacting substances themselves vary continuously, *i.e.* remain in the same state and undergo no allotropic modification. Hence the functions $f(T)$ and $\phi(T)$ have continuous and differentiable first derivatives, and are themselves continuous and differentiable. From the Helmholtz equation

$$A = Q_p + T\left(\frac{\partial A}{\partial T}\right)_p,$$

which is a direct consequence of the two laws of thermodynamics, we obtain

$$\phi(T) = f(T) + T\phi'(T). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Hence $\phi(T)$ and $f(T)$ differ in general by the quantity $T\phi'(T)$, which may be either positive or negative. We shall show later on that $\phi'(T) = -\Sigma S$ is finite at any finite temperature, so that

$$\phi(0) = f(0) \quad \text{or} \quad A_0 = Q_0. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

At the absolute zero the affinity and the heat of reaction are equal to one another. In other words, Berthelot's principle is accurate at the absolute zero.

Differentiating (1), we obtain

$$\phi'(T) = f'(T) + T\phi''(T) + \phi'(T),$$

and hence $$\phi''(T) = -\frac{1}{T}f'(T).$$

Integrating this equation, we obtain

$$\phi'(T) = -\int \frac{1}{T} f'(T)\,dT + C, \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and integrating by parts

$$\phi'(T) = -\frac{f(T)}{T} - \int \frac{f(T)}{T^2}\,dT + C.$$

Substituting (3) in (1), we obtain

$$\phi(T) = -T\int \frac{f(T)}{T^2}\,dT + CT. \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$\phi'(T)$ and $\phi(T)$ can therefore be calculated from $f(T)$ except for the integration constant C. If $\phi(T)$ and $\phi'(T)$ are known for any one temperature (*e.g.* by experimental determination), we

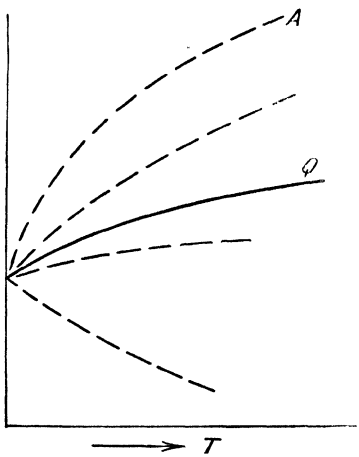


FIG. 42.

can calculate the constant C, and hence also $\phi(T)$ from $f(T)$ for all temperatures.

These consequences of the laws of thermodynamics will become clear from a consideration of Fig. 42. If $Q_p = f(T)$—the continuous curve—is given, the curve $A = \phi(T)$ must intersect with the $f(T)$ curve at the absolute zero. This condition is, however,

fulfilled by any of the dotted curves in the figure. We cannot tell from the form of the $f(T)$ curve alone which of the infinite family of curves represents the real affinity of the reaction. The correct curve is at once determined, however, when one point on the A curve has been obtained from experiment.

2. Nernst's hypothesis for condensed systems.

It is clear from the figure that the A and Q curves might differ appreciably even at temperatures very close to the absolute zero. We know from experiment, however, that Berthelot's principle of the equality of A and Q is generally approximately correct at moderately low temperatures. For this reason Nernst assumed that the A and Q_p curves have a common tangent at the absolute zero, so that

$$\lim_{T=0} f'(T) = \lim_{T=0} \phi'(T). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

We can derive several relationships from this fundamental equation of the theorem.

For the low temperature dT, we have, from (3),

$$\phi'(dT) = -f'(dT) + C. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Equations (5) and (6) are consistent with one another only if

$$(a) \qquad C = 0,$$

and $$(b) \qquad \lim_{T=0} \phi'(T) = \lim_{T=0} f'(T) = 0.$$

These conclusions are, however, valid only for solid or (supercooled) liquid substances which can be cooled to the absolute zero without change of state, for only then do $f(T)$ and $\phi(T)$ remain continuous down to the absolute zero. For reactions between solids and liquids, therefore, the integration constant C is zero, and the reaction involves no change in entropy or in specific heat.

From (4) we now obtain

$$\phi(T) = -T\int \frac{f(T)}{T^2}\, dT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

as the solution of our problem. We are now in a position to calculate the affinity between solid and liquid substances from thermal measurements alone. We shall illustrate the calcula-

tion of $\phi(T)$ from $f(T)$ for condensed systems by two examples of a very general character.

A. Let us assume that the specific heats of all the reacting substances can be expanded in a power series. Their sum $f'(T) = -\Sigma c_p$ can then also be written as a power series, and we obtain $f'(T) = \alpha + \beta T + \gamma T^2 + \dots$.

By Nernst's theorem (equation (6*b*)) we have $\alpha = 0$, and hence

$$f(T) = \int f'(T)\,dT + Q_0,$$

or
$$Q = f(T) = Q_0 + \frac{\beta}{2}T^2 + \frac{\gamma}{3}T^3 ; \quad \dots\dots\dots\dots\dots (8a)$$

and from (7), in a similar manner,

$$A = \phi(T) = -T\int\left(\frac{Q_0}{T^2} + \frac{\beta}{2} + \frac{\gamma}{3}T + \dots\right)$$

$$= Q_0 - \frac{\beta}{2}T^2 - \frac{\gamma}{6}T^3 + \dots \quad \dots\dots\dots\dots\dots (8b)$$

Thus, if the coefficients β and γ are positive, Q_p increases while A diminishes with the temperature. If we are justified

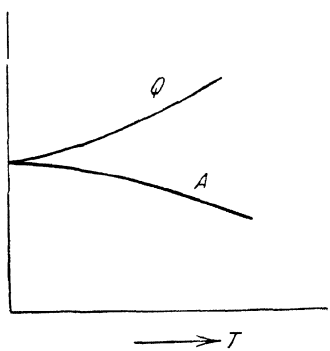


FIG. 43.

in neglecting powers of T higher than the second, the A and Q_p curves will approach their common tangent symmetrically, as shown in Fig. 43.

B. According to Debye's theory (p. 37), the specific heat c_v of a solid body at low temperatures is given by

$$c_v = aT^3,$$

where a is a constant characteristic of the substance.

Neglecting the difference between the specific heat at constant volume and at constant pressure, we obtain

$$f'(T) = -\Sigma a T^3.$$

Integrating this equation, we obtain

$$Q_v = f(T) = Q_{v_0} - \frac{\Sigma a}{4} T^4, \quad \text{.....(9a)}$$

and substituting in (7),

$$\left.\begin{aligned} A = \phi(T) &= Q_{v_0} + T\int -\frac{\Sigma a T^2}{4} dT \\ &= Q_{v_0} + \frac{\Sigma a}{12} T^4. \end{aligned}\right\} \quad \text{.....(9b)}$$

Thus, according to Debye's theory, the Q_v and A curves are not symmetrical with respect to their common tangent even in the neighbourhood of $T = 0$.

The value of the constant a is given by

$$a = \frac{12}{5} \frac{\pi^4 R}{\beta^3 \nu_m^3},$$

where ν_m is the limiting atomic frequency. If Σa is negative, the heat of reaction increases while the affinity diminishes with the temperature, and *vice versa*.

Using Einstein's formula for the specific heat, viz.

$$c_v = 3R\Sigma \frac{e^{\frac{\beta\nu}{T}} \left(\frac{\beta\nu}{T}\right)^2}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2},$$

we can calculate the heat of reaction and the affinity in a similar manner, and obtain

$$Q = Q_0 - 3R\Sigma \left(\frac{\beta\nu}{e^{\frac{\beta\nu}{T}} - 1}\right), \quad \text{.....(10a)}$$

and

$$A = Q_0 + 3\Sigma R\beta\nu - 3RT\Sigma \ln\left(e^{\frac{\beta\nu}{T}} - 1\right). \quad \text{.....(10b)}$$

We may test these equations in several different ways.

1. The specific heats may be determined calorimetrically at various temperatures and the heat of reaction at one (or more) temperatures. From these data we can calculate first $f'(T)$, and

then by integration $f(T)$, and, finally, by equation (7), $\phi(T) = A$. The values calculated at various temperatures can then be compared with experiment.

2. The observed values of $A = \phi(T)$ can be represented by means of an interpolation formula of the form (8*b*) or (10*b*). From the coefficients of the formula we can calculate the values of the difference between the specific heats and of $Q = f(T)$ at various temperatures, and compare them with the experimental values.

3. We can endeavour to find empirical formulae for $f(T)$ and $\phi(T)$, which represent all the experimental observations.

These methods have all been employed with considerable success by Nernst and others. They will be illustrated in the following by a few numerical examples.

To begin with, we shall discuss a deduction from Nernst's heat theorem which is qualitatively in accord with the facts. If the affinity A converges to a finite value A_0 as the temperature is diminished, its second derivative $\frac{d^2A}{dT^2}$ must have the same sign as the first derivative $\frac{dA}{dT}$, as may be seen from Fig. 44. Hence $\frac{dQ}{dT} = -\frac{1}{T}\frac{d^2A}{dT^2}$ must be opposite in sign to $\frac{dA}{dT}$. Thus, if the affinity of a reaction increases with the temperature at low temperatures, the heat of reaction must diminish, and conversely. This consequence of the theorem may readily be tested for reactions whose transition temperature is not too high, *i.e.* reactions for which the affinity A vanishes at a fairly low temperature. Most fusions and solidifications, and also transformations of allotropic modifications of elements and compounds, belong to this type. Let us consider the direction of the reaction to be such that heat is evolved as it proceeds, *e.g.* the solidification of a super-cooled liquid. In this case the affinity diminishes as the temperature is raised $\left(\frac{dA}{dT} < 0\right)$, since A is zero at the melting or transition point, and is positive below it. At the transition point, therefore, $\frac{dQ}{dT}$ must be positive, and consequently the change in specific heat must be negative.

The substances which are formed with evolution of heat (*e.g.* the solid phase) *must therefore always have the smaller specific heat.* This regularity was first discovered by van't Hoff, who confirmed it by the following table.* His proof, however, was based on an erroneous assumption as to the course of the A and Q curves, and must be replaced by Nernst's theorem.

Substance.	$c_{liq.}$	$c_{solid.}$	Substance.	c_{liq}	c_{solid}
Benzene	0·43	0·35	Naphthaline	0·44	0.33
Benzoic acid	0·37	0·27	Naphthylamine	0·39	0.38
Betol	0·27	0·22	Sodium nitrate	0·41	0 28
Lead	0·036	0·034	Nitro naphthaline	0·36	0·28
Bromine	0·11	0·084	Phenylacetic acid	0·49	0·33
Lead chloride	0·1	0·071	Phosphorus	0·2	0·18
Lead iodide	0·065	0·03	Mercury	0·034	0·032
α-Crotonic acid	0·52	0·44	Sulphur	0·24	0·16
Diphenylamine	0·45	0·31	Sulphuric acid	0·085	0·063
p-Dibrom benzene	0·21	0·15	Silver	0·075	0·06
Acetic acid	0·48	0·46	*p*-Toluidin	0·06	0·46
Potassium	0·25	0·17	Water	1	0·5
Potassium nitrate	0·33	0·24	Bismuth	0·036	0·03
Lauric acid	0·53	0·46	Tin	0·064	0·056
Myristic acid	0·54	0·45			

ALLOTROPIC MODIFICATIONS OF ELEMENTS.

Graphite −50°	0·114	Diamond	0·0635
„ 1000°	0·467	„	0·459
Phosphorus (cryst.)	0·17–0·2	Phosphorus (red)	0·17
Sulphur (monoclinic)	0·18	Sulphur (rhombic)	0·16
Tin (white)	0·56	Tin (grey)	0·55

ALLOTROPIC MODIFICATIONS OF COMPOUNDS.

Modification II. is formed with evolution of heat.

	$c_{I.}$	$c_{II.}$
Silver iodide	0·0577	0·0544
Potassium nitrate	0·285	0·203
Ammonium nitrate	0·426	0·355

* Boltzmann, *Festschrift*, 1904, p. 233.

FUSION OF HYDRATED SALTS.

	c_{I}.	c_{II}.
$Na_2S_2O_3 . 5H_2O$ - - -	0·569	0·445
$CaCl_2 . 6H_2O$ - - -	0·56	0·345
$Na_2HPO_4 12H_2O$ - - -	0·734	0·408
$H_2SO_4 . H_2O$ - - -	0·433	0·227
$Ca(NO_3)_2 4H_2O$ - - -	0·519	0·397

Quantitative confirmations of the theorem.

1. Halla* calculated the affinity of the reaction

$$Pb + 2AgCl = PbCl_2 + 2Ag$$

from Brönsted's measurements of the E.M.F. of the cell

$$Pb \quad \begin{matrix} \text{Saturated solution of} \\ PbCl_2 \end{matrix} \mid AgCl \quad Ag.$$

He found that the E.M.F. calculated in calories (volt × 23046) could be expressed very accurately by a formula of the form (8*b*), viz.

$$\phi(T) = E = 11904 - 1{\cdot}0062 \times 10^{-2} T^2 + 8{\cdot}55066 \times 10^{-6} T^3.$$

$T_{\mathrm{abs.}}$	$E_{\mathrm{exp.}}$	$E_{\mathrm{calc\ I.}}$	Diff. %.	$E_{\mathrm{calc.\ II.}}$	Diff. %.
273·0	11·320	11·328	+0·08	11·327	+0·07
289·7	11·271	11·268	−0·03	11·269	−0·02
303·5	11·220	11·217	−0·03	11·220	0·00
322·3	11·153	11·144	−0·09	11·153	0·00
331·3	11·123	11·110	−0·13	11·120	−0·03
340·0	11·084	11·077	−0·07	11·089	+0·05
362·0	10·983	10·992	+0·09	11·008	+0·25

For the heat of reaction we have therefore a corresponding equation of the form (8*a*), viz.

$$f(T) = Q_p = 11904 + 1{\cdot}0062 \times 10^{-2} T^2 - 1{\cdot}710132 \times 10^{-5} T^3.$$

From this equation we find for the heat of reaction at 17° C., $Q_{p\,\mathrm{calc.}} = 12332$ cal., which agrees fairly well with Thomsen's

* *Zeitschr. f. Elektrochem.* **14**, 411 (1908).

experimental value, viz. 12000 cal. We obtain, further, for the change in specific heat,

$$f'(T) = 2{\cdot}0124 \times 10^{-2} T - 5{\cdot}13 \times 10^{-5} T^2.$$

From this we have at

	$\Sigma c_{p\,\text{exp.}}$
$50°$ C. $= 323°$ abs. $\Sigma c_p = 6{\cdot}50 - 5{\cdot}35 = 1{\cdot}15$	1·15
$-83°$ C. $= 190°$ abs. $\Sigma c_p = 3{\cdot}82 - 1{\cdot}85 = 1{\cdot}97$	1·05

The values of $\Sigma c_{p\,\text{exp.}}$ were calculated from the following data :

At 50° C.	At −83° C.
$+\frac{1}{2}$Pb = 3·15	3·03
+AgCl = 13·07	11·77
−Ag = 6·04	5·58
$-\frac{1}{2}$PbCl$_2$ = 9·03	8·20
+1·15	+1·05

Here also the agreement is satisfactory, considering that the specific heats used in the calculation were determined by different observers.

In the above example the heat of reaction was expressed as a power series, in which terms higher than T^3 were neglected. Such a calculation can be at best only approximately correct, as the specific heats of all solid bodies have been shown by recent investigations to diminish much more rapidly at low temperatures than such a formula would indicate. The error is not serious, however, provided the calculation of the affinity A is limited to the range of temperature in which Q_p and $\frac{dQ_p}{dT}$ are accurately represented by the empirical formula. This is shown by the equation see [(1) and (3)]

$$\phi_1(T_1) = f(T_1) + T_1\phi'(T_1) = f(T_1) - T_1\int_0^{T_1} \frac{1}{T} f'(T)dT.$$

The numerical value of the integral depends on the way in which $f'(T)$ varies between zero and the value $f'(T_1)$. The term in which the integral appears is, however, only a relatively small fraction of $\phi(T_1)$, provided the temperature is not too high. The essence of Nernst's theorem is the statement that the thermodynamically indeterminate constant is zero. It would, however,

be better in every case to represent the functions $f(T)$ and $\phi(T)$ by means of the formulae which follow from the theories of Einstein (10*a*) and (10*b*) or Debye.

The formulae (9*a*) and (9*b*) apply only to low temperatures, but the corresponding formulae for higher temperatures can be calculated from Debye's complete specific heat formula (see p. 37).

The calculation is generally somewhat complicated. Using Einstein's formula, Magnus * carried out this calculation for the cell $Pb + 2AgCl = PbCl_2 + 2Ag$, investigated by Brönsted, and obtained the following fairly complicated formula :

$$E = Q_{p_0} + 655 + 3RT\left[ln\left(e^{\frac{58}{T}} - 1\right) + 4\,ln\left(e^{\frac{168}{T}} - 1\right) - 3\,ln\left(e^{\frac{172}{T}} - 1\right) - 2\,ln\left(e^{\frac{162}{T}} - 1\right)\right] - 6{\cdot}45 \times 10^{-5}T^5.$$

The heat of reaction Q_{p_0} was taken to be 12078 cal. By means of this equation the figures under the heading $E_{\text{calc. II.}}$ in the above table were obtained. With the exception of the last figure, the agreement is better than in column $E_{\text{calc. I.}}$

3. Change of state.

A supercooled liquid solidifies when inoculated with a small crystal of the solid, while the latent heat is evolved in the process. The solidification can be performed reversibly and made to yield work by evaporating the liquid at its vapour pressure p_1, allowing the vapour to expand isothermally until the pressure is equal to the vapour pressure p_2 of the solid, and then condensing to the solid state.

The work done in this process is

$$A = RT\,ln\frac{p_1}{p_2} \quad \text{.....(11)}$$

for each mol. solidified. A is the affinity tending to cause the supercooled liquid to solidify. By Nernst's heat theorem this quantity can be calculated from the latent heat of fusion and its variation with the temperature. If the latent heat per mol. is $Q = f(T)$, we have, by (7),

$$A = -T\int \frac{Q}{T^2}dT. \quad \text{.....(12)}$$

* *Zeitschr. f. Elektrochem.* **16**, 273 (1910).

We can draw an important conclusion from a comparison of (11) and (12). For the saturated vapour in equilibrium with the solid and liquid phase, we have, by Clausius' equation, assuming the gas laws for the vapour,

$$\frac{d\ ln\ p_1}{dT} = -\frac{L_1}{RT^2},$$

$$\frac{d\ ln\ p_2}{dT} = -\frac{L_2}{RT^2},$$

where L_1 = heat of vaporisation and L_2 = heat of fusion.

Integrating, we have

$$\log p_1 = -\frac{1}{2{\cdot}3R}\int \frac{L_1}{T^2}\,dT + C_1, \quad \ldots\ldots\ldots\ldots\ldots\ldots (13a)$$

$$\log p_2 = -\frac{1}{2{\cdot}3R}\int \frac{L_2}{T^2}\,dT + C_2. \quad \ldots\ldots\ldots\ldots\ldots\ldots (13b)$$

Substituting (13a) and (13b) in (11), we obtain

$$A = -T\int \frac{W}{T^2}\,dT + C_1 - C_2,$$

since the difference between the heat of sublimation and the heat of vaporisation is equal to the heat of fusion.

This equation is in agreement with (12) only when $C_1 = C_2$; in other words, when the vapour pressure curves of the solid and liquid phases have the same constant.

The correctness of equation (11), which is a consequence of Nernst's theorem, is shown by the example: supercooled water→ice, for which we can calculate the affinity A in both equations (11) and (12). As a first approximation, we may write for the heat of fusion,

$$Q = Q_0 + \frac{\beta}{2}T^2 + \frac{\gamma}{3}T^3. \quad \ldots\ldots\ldots\ldots\ldots\ldots (14a)$$

The affinity is then given by

$$A = Q_0 - \frac{\beta}{2}T^2 - \frac{\gamma}{6}T^3. \quad \ldots\ldots\ldots\ldots\ldots\ldots (14b)$$

Three equations are necessary for the determination of the

constants Q_0, β, and γ. We may take for this purpose the latent heat at 0° C., $Q_{273} = 80$ cal., the difference between the specific heats of water and ice at 0° C.,

$$\frac{dQ}{dT} = \beta T + \gamma T^2 = 0{\cdot}498,$$

and, finally, the condition that the affinity must be zero at the melting point. We have therefore the three equations

$$80 = Q_0 + \frac{\beta}{2} \times 273^2 + \frac{\gamma}{3} \times 273^3,$$

$$0{\cdot}498 = \beta \times 273 + \gamma \times 273^2,$$

$$0 = Q_0 - \frac{\beta}{2} 273^2 - \frac{\gamma}{6} 273^3;$$

and hence

$$Q_0 = 30{\cdot}7,$$

$$\beta = 3{\cdot}22 \times 10^{-4},$$

$$\gamma = 5{\cdot}50 \times 10^{-6}.$$

From these values A_1 has been calculated in the table below. The figures under A_2 were obtained by equation (11) from the determinations of Scheel and Heuse.*

°C.	A_1.	A_2.
−5	1·4 cal.	1·43
−10	2·8 „	2·77
−15	4·15 „	4·06
−20	5·6 „	5·65

The agreement between the two columns is excellent.†

Vapour pressure curves. The general form of the vapour pressure curves is given by equations (13). All empirical equations which have yet been proposed (for the literature, see Winkelmann, vol. iii. p. 903 *et seq.*) must therefore coincide with the complete equation for all temperatures at which they are in agreement with experiment. The vapour pressure curve of a

* *Ann. d. Phys.* **29**, 723 (1909).

† See also J. T. Barker, *Zeitschr. f. physik. Chemie*, **71**, 235 (1910).

pure substance is not determined by thermal quantities alone (such as the latent heat and the specific heats of the liquid and vapour). In order to calculate the vapour pressures at all temperatures, we must either know the value of the constant C (which is not determined by thermal quantities) or the value of the vapour pressure at any one temperature. The numerical determination of this constant, which at once enables us to calculate the vapour pressure curves of both solid and liquid phases (by Nernst's theorem) is therefore of great importance. Unfortunately, it is not yet possible to obtain the exact value of this important quantity for any substance.

It is not sufficient even for an approximate calculation to know the form of the function L for a limited range of temperature (see p. 407). The value of the constant C depends to a considerable extent on the form of the function L at very low temperatures. For the calculation of C it is therefore necessary to know the values of the specific heats at very low temperatures. These have recently been determined in Nernst's laboratory for a number of solid substances, but unfortunately almost exclusively for substances which volatilise only at very high temperatures. Iodine is apparently the only substance whose vapour pressure and specific heats at low temperatures are both known. In this case the vapour pressure constant c can therefore be calculated with a certain degree of approximation. The calculation is as follows:

The specific heat of solid iodine, according to Nernst and Lindemann * is given by

$$c = \tfrac{3}{2}R\left[\frac{\left(\frac{\beta\nu}{T}\right)^2 e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}}-1\right)^2}+\frac{\left(\frac{\beta\nu}{2T}\right)^2 e^{\frac{\beta\nu}{2T}}}{\left(e^{\frac{\beta\nu}{2T}}-1\right)}\right],$$

where $\beta\nu = 100.$

The molecular specific heat of iodine vapour c_p is $3{\cdot}5R$ according to the kinetic theory. At room temperature it is somewhat higher than this, but we shall neglect this increase, as it probably

* *Zeitschr. f. Elektrochem.* **17**, 817 (1911). The difference between c_p and c_v has been neglected for this approximate calculation.

does not occur until moderately high temperatures. Thus we obtain

$$\frac{dL}{dT}=3R\left[\frac{\left(\frac{100}{T}\right)^2 e^{\frac{100}{T}}}{\left(e^{\frac{100}{T}}-1\right)^2}+\frac{\left(\frac{50}{T}\right)^2 e^{\frac{50}{T}}}{\left(e^{\frac{50}{T}}-1\right)^2}\right]=3{\cdot}5R,$$

where L is the latent heat of evaporation per mol. of I_2 ($L<0$).

Integrating, we have

$$L=3R\int[\quad]dT-3{\cdot}5RT+\text{const.}$$

$$=L_0+3R\left[\frac{100}{e^{\frac{100}{T}}-1}+\frac{50}{e^{\frac{50}{T}}-1}\right]-3{\cdot}5RT.$$

Combining this with (13a), we obtain

$$\log p=-\frac{1}{2{\cdot}3R}\int\frac{L}{T^2}dT+C$$

$$=\frac{L_0}{2{\cdot}3RT}-\frac{3}{2{\cdot}3}\int\frac{1}{T^2}[\quad]dT+3{\cdot}5\log T+C$$

$$=\frac{L_0}{4{\cdot}57T}-\frac{3}{2{\cdot}3}\frac{100}{T}+3\log\left(e^{\frac{100}{T}}-1\right)-\frac{3\times 50}{2{\cdot}3T}+3\log\left(e^{\frac{50}{T}}-1\right)$$

$$+3{\cdot}5\log T+C.$$

This equation contains only the two constants L_0 and C, which can therefore be calculated if we know the value of the vapour pressure of solid iodine at two temperatures. According to Ramsay and Young,* we have:

At $T_1=387°$ abs., $p=90$ mm. $=0{\cdot}1182$ atm.,
and at $T_2=358°$ abs., $p=20$ mm. $=0{\cdot}0262$ atm.

Hence we obtain the two equations

$$-0{\cdot}937=\frac{L_0}{4{\cdot}57\times 387}-\frac{450}{2{\cdot}3\times 387}+3(\log 0{\cdot}296+\log 0{\cdot}138)$$

$$+3{\cdot}5\times 2{\cdot}588+C,$$

or $$-5{\cdot}31=\frac{L_0}{1768}+C,$$

* *Journ. Chem. Soc.* London, **49**, 453 (1886).

and

$$-1{\cdot}582=\frac{L_0}{4{\cdot}57\times358}-\frac{450}{2{\cdot}3\times358}+3(\log 0{\cdot}322+\log 0{\cdot}150)$$
$$+3{\cdot}5\times2{\cdot}544+C,$$

or $$-6{\cdot}02=\frac{L_0}{1636}+C.$$

Solving these equations, we have

$$0{\cdot}71=\frac{L_0}{1768}-\frac{L_0}{1636},$$

i.e. $$L_0=-\frac{0{\cdot}71\times1768\times1636}{132}=-15600 \text{ cal.},$$

and $$C=3{\cdot}5.$$

Hence the complete equation for the vapour pressure of iodine in atmospheres is

$$\log p=-\frac{15600}{4{\cdot}57T}-\frac{450}{2{\cdot}3T}+3\left[\log\left(e^{\frac{100}{T}}-1\right)+\log\left(e^{\frac{50}{T}}-1\right)\right]$$
$$+3{\cdot}5\log T+3{\cdot}5$$
$$=-\frac{3600}{T}+3\left[\log\left(e^{\frac{100}{T}}-1\right)+\log\left(e^{\frac{50}{T}}-1\right)\right]+3{\cdot}5\log T+3{\cdot}5.$$

By means of this equation we can calculate the vapour pressure of iodine down to considerably lower temperatures than those taken for the calculation of L_0 and C. The following table contains the calculated and experimental values. The agreement is very good down to very low temperatures :

VAPOUR PRESSURE OF IODINE.

+ °C.	$p_{calc.}$	$p_{exp.}$	
−40·7	0·00026 mm.	0·00022 mm.	*
−20·9	0·0040 „	0·0025 „	*
0	0·036 „	0·027 „	*
10	0·10 „	0·06 „	†
30	0·51 „	0·60 „	†
40	1·1 „	1·16 „	†
50	2·3 „	2·35 „	†
60	4·4 „	4·42 „	†

* Naumann, *Dissert.* Berlin (1907).

† Stelzner and Niederschulte, *Verhandl. d. deutsch. phys. Gesellsch.* **7**, 159 (1905).

We shall show in the next paragraph that the vapour pressure constants play an important part in the calculation of chemical equilibria in gases. The first problem which Nernst had to solve after the discovery of his theorem was therefore the calculation of at least the approximate value of C for as many simple substances as possible. For this purpose he made use of the theorem of corresponding states, and assumed further that the specific heat of solid and liquid bodies diminishes to a small but finite value (viz. $n \times 1{\cdot}5$, where n is the number of atoms in the molecule) as the temperature is lowered. On the evidence of the measurements published up to that time he also assumed that the molecular specific heat c_p of gases and vapours is a linear function of the temperature which approaches the value $3{\cdot}5 + n \times 1{\cdot}5$ at very low temperatures. In this way he arrived at the vapour pressure formula

$$\log p = \frac{L_0}{2{\cdot}3RT} + \frac{3{\cdot}5}{R} \log T - \frac{\epsilon}{2{\cdot}3R} T + C,$$

which is confirmed by experiment for a wide range of temperature in a large number of cases.* By means of this formula he calculated the following table for C : †

Substance.	C.	Substance.	C.
H_2	1·6	CO_2	3·2
CH_4	2·5	CS_2	3·1
N_2	2·6	NH_3	3·3
O_2	2·8	H_2O	3·6
CO	3·5	CCl_4	3·1
Cl_2	3·1	$CHCl_3$	3·2
J_2	3·9	C_6H_6	3·0
HCl	3·0	C_2H_5OH	4·1
NO	3·5	$(C_2H_5)_2O$	3·3
N_2O	3·3	CH_3COCH_3	3·7
H_2S	3·0	Propyl acetate	3·8
SO_2	3·3		

The value for iodine (3·9) given by Nernst is not very different from that calculated above (3·5) by the more exact equation. We may therefore assume that the other values of C given by Nernst are at least approximately correct. They may therefore

* For a detailed discussion of this formula, see Nernst, *Thermodynamics in Chemistry*, p. 53 *et seq.*

† *Lehrbuch*, 6th edition, p. 708.

be employed in rough calculations, provided Nernst's assumptions with regard to the specific heats are adhered to throughout the calculation.

4. Application of the theorem to gas reactions.

As gases cannot be cooled continuously to the absolute zero without change of state, the equations for the affinity calculated in the preceding paragraph can have no significance for reactions in gases. We must therefore return again to equation (4) in the form

$$A = \phi(T) = -T\int \frac{Q}{T^2} dT + CT.$$

The integration constant need not be zero, and will in general have a finite value varying from case to case. The value of C cannot be calculated from thermal quantities. We can calculate this constant, however, for every reaction, as Nernst has shown, by adding the vapour pressure constants of the reacting substances.

To prove this, let us consider the maximum work which can be obtained from a gas reaction at temperature T. We shall choose this temperature so low that the reacting substances are all far from their critical point, and shall therefore assume that their saturated vapours obey the simple gas laws approximately. We can then carry out the reaction reversibly in two ways. First, as described in Chapter IX. p. 317. Second, by compressing the gases isothermally from the original pressures p_1, p_2, ..., to the pressures p_1', p_2', ..., which correspond to the pressures of the saturated vapours in equilibrium with the solid or liquid phases. Then condensing isothermally and allowing the reaction to take place reversibly in the condensed system, and finally evaporating the products of the reaction isothermally and expanding them to the partial pressures which they would have exerted if the reaction had taken place at constant pressure between the gases.

The work done in these two reversible and isothermal processes must be equal to one another. The work done in the first process (see p. 318) is

$$w = RT\ ln\ K_p - RT\Sigma\ ln\ p + \nu RT,*$$

* $RT\ ln\ K_p - RT\Sigma\ ln\ p$ is the maximum work obtainable less the work necessarily done against the external pressures, owing to the change in volume; ν is the increase in the number of mols. consequent on the reaction.

where K_p is the equilibrium constant and the summation is to be extended over the initial and final pressures p. The substances which are formed with evolution of heat are reckoned positive and the remainder negative in the summation.

The work done in the second process may be calculated as follows:

1. In compressing from the initial pressures p to the saturation pressures p', and in expanding the products of reaction from p' to p, the work gained is

$$w_1 = RT\Sigma \ln \frac{p'}{p}.$$

2. In condensing the substances originally present, and evaporating the products of the reaction, the work done by the system is

$$w_2 = +\nu RT.$$

This is the work necessarily done against the external pressures owing to the change in volume.

3. The work done by the condensed system during the reversible reaction can be calculated by Nernst's heat theorem from thermal quantities alone. It is

$$w_3 = -T\int \frac{Q'}{T^2}\,dT,$$

where Q is the heat of reaction in the condensed system. The total work done is therefore $w = w_1 + w_2 = w_3$, and hence

$$RT \ln K_p = RT\Sigma \ln p' - T\int \frac{Q'}{T^2}\,dT. \quad \ldots\ldots\ldots\ldots\ldots(15)$$

Substituting in this equation (15) the values of $\ln p'$ given by (13), we obtain

$$RT \log K_p = \frac{T}{2{\cdot}3}\int \frac{\Sigma L + Q'}{T^2}\,dT + RT\Sigma C.$$

$\Sigma L + Q'$, *i.e.* the sum of all the latent heats of evaporation and sublimation, and the heat of reaction in the condensed system, is equal to the heat of the reaction at constant pressure in the gaseous system. Hence we obtain

$$RT \log K_p = -\frac{T}{2{\cdot}3}\int \frac{Q_p}{T^2}\,dT + RT\Sigma C, \quad \ldots\ldots\ldots\ldots(16)$$

or $$\log K_p = -\frac{1}{2{\cdot}3R}\int \frac{Q_p}{T^2}\,dT + \Sigma C, \quad \text{.....(16}a\text{)}$$

as the integral of van't Hoff's differential equation (see p. 305, equation (5a)) $$\frac{d\ ln\ K_p}{dT} = -\frac{Q_p}{RT^2}.$$

The integration constant of this equation left undetermined by thermodynamics is therefore the sum of the vapour pressure constants of the individual reacting substances. In this way it is possible in principle to calculate chemical equilibria at all temperatures from thermal quantities (calorimetric measurements) and vapour pressure measurements with the individual reacting substances.

Comparing equation (16a) with equations (10) and (11a) on p. 307, we find that the thermodynamically undetermined integration constant of van't Hoff's equation (reckoning with partial pressures instead of concentrations) is given by

$$\Sigma C = \frac{J'}{2{\cdot}3} = \frac{J + \nu\ ln\ R}{2{\cdot}3} = \Sigma\frac{(S' - c_{p_0}) + \nu R\ ln\ R}{2{\cdot}3R},$$

and hence $$S' = 2{\cdot}3R(C - \log R) + c_{p_0}. \text{*} \quad \text{.....(16}b\text{)}$$

Thus Nernst's heat theorem enables us to calculate the entropy constant of a gas from its specific heat and from the vapour pressure curve of the condensed gas, and *vice versa*. Equation (16b), however, involves the assumption that the specific heat of the gas can be expressed as a series of powers of T.

In comparing equation (16a) with experiment, we must remember that the assumptions made by Nernst in calculating the values of C must also be used in calculating Q. By doing so we compensate partially, at least, for the errors due to our ignorance of the specific heats at lower temperatures. In using Nernst's values of C, we must therefore always assume that the specific heat of a gas (see p. 414) is given by

$$c_p = 3{\cdot}5 + n \times 1{\cdot}5 + aT.$$

We have therefore

$$\frac{dQ}{dT} = -\Sigma c_p = -\nu \times 3{\cdot}5 - \Sigma aT.$$

* This may also be written $S_p' = 2{\cdot}3RC - c_{p_0}$ (see note, p. 307).

Σn vanishes since the total number of atoms is unaltered by the reaction. Integrating, we have

$$Q = Q_0 - \nu \times 3{\cdot}5 \times T - \frac{\Sigma a T^2}{2},$$

and by (16a),

$$\log K_p = \frac{Q_0}{2{\cdot}3RT} + \frac{\nu \times 3{\cdot}5}{R} \log T + \frac{\Sigma a T}{2 \times 2{\cdot}3R} + \Sigma C. \quad \ldots\ldots(17)$$

The constant Q_0 can be expressed in terms of the known heat of reaction Q_{T_1} at the temperature T_1 (generally room temperature). Thus we have

$$Q_0 = Q_{T_1} + \nu \times 3{\cdot}5 T_1 + \frac{\Sigma a}{2} T_1^2,$$

and hence

$$\log K_p = \frac{Q_{T_1}}{2{\cdot}3RT} + \frac{3{\cdot}5\nu}{R}\left(\log T + \frac{T_1}{2{\cdot}3T}\right) + \frac{\Sigma a}{2 \times 2{\cdot}3R}\left(T + \frac{T_1^2}{T}\right) + \Sigma C. \quad (17a)$$

The equilibrium constant can therefore be calculated for all temperatures when the vapour pressure constant, the heat of reaction at a given temperature, and, finally, the temperature coefficients of the specific heats (and hence Σa) are given. For the formation of water vapour from the elements, the calculation is as follows:

We have for $T = 273$,

$$Q_{273} = +116200 \text{ cal. (for 2 mols. of } H_2O),^*$$

and
$$2c_{p_{H_2O}} - 2c_{p_{H_2}} - c_{p_{O_2}} = 2 \times 7{\cdot}9 - 3{\cdot}68 = -4{\cdot}6,^\dagger$$

$$\nu = -1,$$

and hence
$$-4{\cdot}6 = -3{\cdot}5 + \Sigma a \times 273,$$

$$\Sigma a = \frac{-1{\cdot}1}{273} = -0{\cdot}004,$$

$$\Sigma C = 2 \times 3{\cdot}6 - 2 \times 1{\cdot}6 - 2{\cdot}8 = +1{\cdot}2,$$

and therefore

$$\left.\begin{aligned} \log K_p &= \frac{116200}{4{\cdot}57T} - 1{\cdot}75\left(\log T + \frac{119}{T}\right) \\ &\quad - 0{\cdot}00043\left(T + \frac{7{\cdot}45 \times 10^4}{T}\right) + 1{\cdot}2 \\ &= \frac{25200}{T} - 1{\cdot}75 \log T - 0{\cdot}00043 \times T + 1{\cdot}2. \end{aligned}\right\} \quad \ldots(17b)$$

* *Abegg's Handbuch*, i. p. 81. † According to Langen (*ibidem*).

The following table contains the values calculated from this equation compared with the experimental determinations: *

T.	$\log K_{p\,\text{calc.}}$	$\log K_{p\,\text{exp.}}$
1300	14·55	14·00
1500	11·8	11·41
1705	9·6	9·28
2155	6·15	6·09
2300	5·3	5·06

Considering the somewhat daring assumptions made with regard to the variation of the specific heats, the agreement is excellent. Nernst has calculated many other chemical equilibria in this way from the vapour pressure constants and thermal quantities, and has obtained a complete confirmation of his theory.

Comparing equations (17*b*) and (12), p. 310, which are both approximately in accord with experiment, we obtain the following equations:

$$(a) \qquad \log K_p = \frac{24800}{T} - 2{\cdot}5 \log T + 2{\cdot}8,$$

and $$(b) \qquad \log K_p = \frac{25200}{T} - 1{\cdot}75 \log T - 0{\cdot}00043T + 1{\cdot}2.$$

In (*a*) the linear term in T does not appear, since the variation of the specific heats is not taken into account. The terms in $\log T$ differ by a constant factor, since the specific heats of the gases were calculated from the kinetic theory in (*a*), while in (*b*) Nernst's formula $c_p = 3{\cdot}5 + n \times 1{\cdot}5 + aT$ was used. The constants of the two equations are therefore different. As both equations are equally well confirmed by experiment, we might at first sight suppose them to have equal theoretical significance. Equation (*b*) is, however, much the more valuable of the two, as the numerical values of its constants can be calculated from measurements with the pure substances which take part in the reaction, while in (*a*) a determination of the equilibrium is necessary. Nernst's equation (*b*) is superior to the older equation, in that it enables

* See p. 311

us to calculate the approximate position of the equilibrium in advance for all temperatures without a single actual determination of the equilibrium.

Approximate equations. For a first rough calculation of the position of an equilibrium it is sufficient in most cases, according to Nernst, to use a somewhat simplified form of equation (17). As a rule α is very small—for reactions between simple gases at least—and at high temperatures $\frac{T_1}{2{\cdot}3T}$ may be neglected in comparison with $\log T$. As the value of C for most simple gases and vapours is in the neighbourhood of 3·0, equation (17) may be simplified to

$$\log K_p = \frac{Q}{4{\cdot}6T} + \nu \times 1{\cdot}75 \log T + 3\nu. \quad \ldots\ldots\ldots\ldots (18)$$

By means of this simple equation we can calculate the approximate position of the equilibrium from the heat of reaction at room temperature.

The value of this equation is shown in the following by its application to a few technically important reactions :

1. The formation of sulphur trioxide from sulphur dioxide and oxygen.

According to Berthelot, we have $Q = +45200$ cal. (for $2SO_3$), so that

$$\log K_p = \frac{45200}{4{\cdot}6T} - 1{\cdot}75 \log T - 3{\cdot}0,$$

and hence, for $T = 800° = 527°$ C.,

$$\log K_p = 12{\cdot}3 - 5{\cdot}07 - 3{\cdot}0 = 4{\cdot}2.$$

The degree of dissociation of SO_3, x, at a total pressure of one atmosphere is therefore given by

$$\frac{p^2SO_3}{p^2_{SO_2} \cdot p_{O_2}} = \left(\frac{1-x}{1+\frac{x}{2}}\right)^2 \cdot \frac{\left(1+\frac{x}{2}\right)^3}{x^3} \times 2 = \frac{2(1-x)^2\left(1+\frac{x}{2}\right)}{x^3} = 10^{4{\cdot}2}.$$

x is therefore small in comparison with unity, so that

$$x^3 = 2 \times 10^{-4{\cdot}2},$$

$$x = 0{\cdot}05.$$

According to this, SO_3 should be dissociated 5 per cent. at 527° C. and a pressure of one atmosphere. This is in agreement with technical experience, as the temperature in the contact process (with platinum as catalyst) must not exceed 450°. According to the accurate measurements of Bodenstein and Pohl,* the degree of dissociation of SO_3 at 500° is 8·7 per cent.

2. The dissociation of CO_2 according to the equation

$$2CO_2 = 2CO + O_2.$$

In this case we have $Q = 136000$ cal., $\nu = -1$, and hence

$$\log K_p = \frac{29600}{T} - 1{\cdot}75 \log T - 3.$$

For $T = 1800° = 1527°$ C., we have therefore

$$\log K_p = \frac{29600}{1800} - 1{\cdot}75 \times 3{\cdot}255 - 3 = +7{\cdot}7.$$

Hence, from $$\log K_p = \log \frac{2}{x^3} = 7{\cdot}7,$$

we obtain $$x = 0{\cdot}0034.$$

According to the approximate equation, the dissociation is therefore 0·34 per cent. at 1527° C. in good agreement with the experimental value found by Lowenstein † ($x = 0{\cdot}4$ per cent. at 1500° C.).

3. *The formation of nitric oxide.* $N_2 + O_2 = 2NO$. For reactions which involve no change in volume, we have $\nu = 0$, and hence

$$\log K = \frac{Q}{RT}.$$

Here we have $Q = 43200$, and hence

$$\log K = \log \frac{[N_2][O_2]}{[NO]^2} = \frac{9400}{T}.$$

Thus, for $T = 1800°$ abs. we have $\log K = 5{\cdot}2$. From this we calculate the maximum amount of NO formed in air at 1800° abs. to be

$$x = 0{\cdot}001 = 0{\cdot}1 \text{ per cent.},$$

since $$\log \frac{0{\cdot}8 \times 0{\cdot}2}{x^2} = 5{\cdot}2.$$

* *Zeitschr. f. Electrochemie*, **11**, 385 (1905).

† *Zeitschr. f. physikal. Chemie*, **54**, 715 (1906).

This is also approximately in agreement with experience, as the yield of NO at the somewhat higher temperature $T = 1811°$ was found to be 0·37 per cent.*

5. Heterogeneous equilibria.

In Chapter IX. § 6, we showed that the affinity of reactions between solids and gases could be calculated in exactly the same way as the affinity between gases alone. If p, p_1, etc., are the partial pressures at which the gases are in equilibrium with the solid substances, the affinity between the gases under atmospheric pressure and the solid substances is again given by

$$A = -RT\Sigma \ln p.$$

By (4), p. 415, we have also

$$A = -T\int \frac{Q}{T^2}\,dT + T \times \text{const.}$$

By the method used on p. 416 for pure gas reactions, Nernst has shown that the integration constant can again be expressed as the sum of the vapour pressure constants of the individual volatile reacting substances. In most of the more important heterogeneous reactions only a single gas takes part in the reaction, as, for example, in the dissociation of carbonates, hydroxides, ammoniates, salt hydrates, and, further, in reactions between metals and oxygen or the halogens. In these cases the condition for equilibrium simplifies to

$$\Sigma \ln p = \frac{1}{R}\int \frac{Q}{T^2}\,dT - \Sigma C,$$

$$\log p = \frac{1}{2{\cdot}3R}\int \frac{Q}{T^2}\,dT \pm C.$$

Q is the heat evolved in the formation of 1 mol. of the gas (usually <0). C is positive when the gas is formed with absorption of heat, and conversely. In applying this equation to numerical calculations, the restrictions mentioned on p. 417 for pure gas reactions must be observed here also. If Nernst's

* Nernst, *Zeitschr. f. anorg. Chemie*, **49**, 213 (1906).

values of the vapour pressure constant C are employed, the formula

$$Q = Q_0 + 3{\cdot}5T - \frac{\Sigma\alpha}{2}T^2 \text{ (since } \nu = -1)$$

must be used for the heat of reaction.

For dissociations of solid bodies in which only one gaseous element or compound is produced, we have therefore the equation

$$\log p = \frac{-Q_0}{2{\cdot}3RT} + \frac{3{\cdot}5}{R}\log T - \frac{\Sigma\alpha}{2{\cdot}3\times 2R}T + C,$$

or substituting the known heat of reaction Q_{T_1} at the temperature T_1 for the constant Q_0 (as on p. 418), we have

$$\log p = \frac{-Q_{T_1}}{2{\cdot}3RT} + \frac{3{\cdot}5}{R}\left(\log T + \frac{T_1}{2{\cdot}3T}\right) - \frac{\Sigma\alpha}{2{\cdot}3\times 2R}\left(T + \frac{T_1^2}{T}\right) + C.$$

Numerical example. According to Thomsen and de Forcrand, we have, for the formation of $CaCO_3$ from CaO and CO_2,

$$Q_{300} = 42900 \text{ (mean value)},$$

and, further, at 300° abs.,

$$c_{CaCO_3} - c_{CaO} - c_{CO_2} = 20{\cdot}3 - 10{\cdot}2 - 9{\cdot}0 = 1{\cdot}1.$$

Hence
$$-\frac{dQ}{dT} = -3{\cdot}5 + \Sigma\alpha \times 300 = 1{\cdot}1,$$

and therefore
$$\Sigma\alpha = +0{\cdot}0153.$$

From these data we obtain

$$\log p = \frac{-9370}{T} + 1{\cdot}75\left(\log T + \frac{130}{T}\right) - 0{\cdot}0017\left(T + \frac{9\times 10^4}{T}\right) + C$$

$$= \frac{-9160}{T} + 1{\cdot}75\log T - 0{\cdot}0017T + 3{\cdot}2.$$

For $T = 1000°$ abs. $= 727°$ C. we have by this equation

$$\log p = -2{\cdot}4, \quad p = 0{\cdot}004 \text{ atm.} = 3{\cdot}0 \text{ mm.}$$

The dissociation pressure of $CaCO_3$ must therefore be measurable at this temperature. The experimental value is somewhat higher, viz. 44 mm.*

* Johnston, *Journ. Amer. Chem. Soc.* **32**, 938 (1910).

This discrepancy is, however, not to be attributed to the invalidity of Nernst's heat theorem, but to the obvious inaccuracy of the assumptions regarding the specific heats. Two solids and only one gas take part in the reaction, and the error made in the calculation of C is apparently not nearly so completely eliminated as in pure gas reactions.

For this reason we may dispense with the linear term in T, and use the approximate equation

$$\log p = \frac{-Q}{4{\cdot}6T} + 1{\cdot}75 \log T + 3{\cdot}0 \quad \ldots\ldots\ldots\ldots\ldots\ldots (19)$$

to obtain a rough estimate of the position of the equilibrium.

In the following table (due to Brill *) the calculated and observed values of the temperature T_0 at which the dissociation pressure reaches one atmosphere (so that $\log p = 0$) are given, and show the approximate validity of equation (19).

Substance.	Q.	$T_{0\,\text{calc.}}$	$T_{0\,\text{exp.}}$
Ag_2CO_3	20000	548	498
$PbCO_3$	22580	610	575
$MnCO_3$	23500	632	600 (approx.)
$CaCO_3$	42520	1091	1098
S_2CO_3	55770	1403	1428

The calculated dissociation temperatures corresponding to various heats of dissociation are as follows :

Q.	$T_{0\,\text{calc.}}$	Q.	$T_{0\,\text{calc.}}$
10000	300	75000	1900
20000	550	100000	2450
30000	800	150000	3500
40000	1050	200000	4650
50000	1300	300000	6800

This table shows that even those solid compounds which have a very high heat of formation, and are therefore regarded as very stable, must all be dissociated at the temperature of a hot blowpipe flame or of the electric arc or spark. In reality most

* *Zeitschr. f. physikal. Chemie*, **57**, 736 (1906).

solids, *e.g.* metallic salts, are decomposed at much lower temperatures than those indicated in the table. This is due to the fact that the compounds themselves as well as their dissociation products are all volatile at high temperatures. The figures in the table are therefore only an upper limit for the stability of compounds. These facts are of importance for the theory of the production of spectra.

According to Nernst, equations (18) and (19) can be used in place of Berthelot's principle as a criterion of the stability of compounds. We see from these equations that the stability of a compound is greater the higher its heat of formation and the smaller the change in volume produced by its dissociation. (Q and ν are generally opposite in sign.) Ammonia, for example, splits up into its elements at a few hundred degrees centigrade in spite of its comparatively great heat of formation, because the dissociation is accompanied by a considerable increase in volume.

In a similar manner we can account for the ease with which the ammonium halides decompose, while the corresponding hydrogen halides, which are formed without change in volume, are relatively very stable. For organic compounds we conclude that hydrocarbons of high molecular weight, such as benzene, cannot be stable relative to carbon and hydrogen, but must tend to split up into their elements even when the heat of formation is positive. Acetylene, on the other hand, which is formed from C and H_2 without change in volume, can only be formed at very high temperatures (*e.g.* in the electric spark) on account of its negative heat of formation, and decomposes into carbon and hydrogen at moderate temperatures as soon as the temperature is high enough to permit the decomposition to take place with appreciable velocity. A great many organic compounds are only known to us on account of the extreme slowness with which they decompose at ordinary temperatures.*

6. General discussion of Nernst's heat theorem.

In the foregoing paragraphs we have followed for the most part Nernst's line of thought in the development of his heat

* Further applications of these principles will be found in a treatise by Pollitzer (Ahrens-Hertz, *Sammlung chem.-techn. Vorträge*, 1912).

theorem. From an hypothesis regarding the relationship between the affinity and the heat evolved in chemical reactions, at very low temperatures, consistent with the laws of thermodynamics but not deducible from them, deductions have been made which are valid for all temperatures, and can therefore be tested by experiment. The result of this test has been favourable throughout, so that we may now regard Nernst's theorem as practically confirmed by experiment.*

Even in its original form the theorem deals with chemical reactions and changes of state, that is to say, with the most important natural phenomena accompanied by evolution or absorption of heat. It is therefore natural to suspect that the heat theorem, like the two laws of thermodynamics, has its origin in the nature of heat itself. The laws of thermodynamics, as was shown in Chapters III. and V., could be traced back to the results of our everyday experience (impossibility of perpetual motion of the first and second kinds). This simple method of derivation fails in the case of the new theorem because temperatures in the neighbourhood of the absolute zero can never be the immediate objects of experience. They can only be reached by refined experimental methods. For this reason Nernst's theorem can never be susceptible of direct experimental proof, and can only be tested by its consequences. We can deduce the theorem, however, from a more general principle regarding the nature of heat and the properties of the thermodynamic functions.

This derivation must naturally be based on the properties which we attribute to the absolute zero of the temperature scale. Leaving the kinetic theory of heat for the moment out of account, we can characterise the absolute zero only by the state of a body in which its heat energy is zero. We know by experience that the passage of heat from higher to lower temperatures by radiation and conduction can never be entirely eliminated, so that the absolute zero can never be completely attained. We can only approach it more or less closely. The absolute temperature zero

* So far the only objections to the principles involved in Nernst's Theorem are those raised by Kohnstamm and Ornstein (*Akad. d. Wetenschapen*, Amsterdam, Dec. 1910 and Feb. 1912. See also Nernst, *ibidem*, June 1911).

is therefore a limiting conception, and is essentially different from all other temperatures.

Thus, if we plot against the temperature any property of a body which varies with the temperature, the graph always shows this exceptional nature of the absolute zero. The temperature can never be negative, so that the curve cannot be prolonged beyond the absolute zero. The only types of curve which appear to occur in nature are the continuous curves *a*, *b*, *c* in Fig. 44.

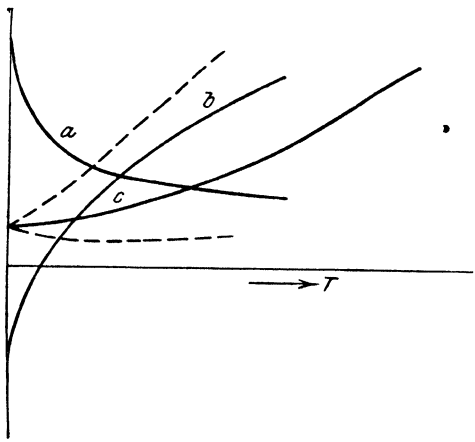


FIG. 44.

The curve therefore either becomes positively or negatively infinite or converges gradually to a finite limiting value. Any other form of curve for which the differential coefficient does not become zero or infinite at the absolute zero (such as the dotted curves in the figure) appears to be incompatible with the unique character of the absolute zero, compared with all other temperatures. We have therefore a considerable amount of justification for the hypothesis that *the temperature coefficient of any property of a body which varies with the temperature and approaches a finite limiting value as the temperature is lowered is zero.*

We cannot, however, tell beforehand whether a given property will be finite at the absolute zero or whether it will become positively or negatively infinite.

This can only be decided by experiment, or, failing that, by a suitable hypothesis whose consequences are in agreement with experiment. Properties which appear to approach infinity at the absolute zero are, for example, the electrical and thermal conductivity of metals and the thermal conductivity of crystals (Eucken *), while the thermal conductivity of amorphous bodies, the specific heat, and the coefficient of expansion appear to approach zero.

Let us consider a few of the properties of homogeneous substances.

The volume of a body diminishes as the temperature is lowered, and approaches a definite limiting value v_0. Hence, by our hypothesis $\lim_{T=0}\left(\frac{dv}{dT}\right)=0$. In words, the coefficient of expansion of all bodies diminishes as the temperature is lowered and converges towards zero. Since the volume v_0 is finite it follows likewise that the compressibility of the body, x, also remains finite at the absolute zero. Hence $\frac{dx}{dT}$ must also converge towards zero as the temperature is lowered, *i.e.* the temperature coefficient of the compressibility becomes smaller and smaller as we approach the absolute zero.

As far as one can judge from the experimental evidence, our hypothesis is confirmed in both cases

$$\left(\text{viz. } \lim_{T=0}\frac{dv}{dT}=0 \quad \text{and} \quad \lim_{T=0}\frac{dx}{dT}=0\right). \dagger$$

The energy U of a body is the sum of two parts, viz. the heat energy and the so-called volume energy, the increment of which is the work done in an isothermal compression. As the volume and the compressibility are both finite at the absolute zero, while the heat energy approaches zero, it follows that the total energy U must be finite at the absolute zero, and hence that $\lim_{T=0}\frac{dU}{dT}=0$. Our hypothesis therefore leads us to the important result that the specific heat of all substances approaches zero

* *Annalen d. Physik*, **34**, 185 (1911).

† See Gruneisen, *Ann. d. Physik*, **33**, 75 (1910); cf. also p. 166.

as the temperature is lowered. This result is in accord with the recent theories of Einstein and Debye* (see p. 37) and with the experimental researches of Nernst.

The entropy S, like the energy U, is a function of volume and temperature. It is not, however, possible without further assumption to predict the nature of the S-T curve in the neighbourhood of the absolute zero. By the definition of entropy we have

$$dS = \frac{dQ_v}{T} = \frac{dU}{T} + p\frac{dv}{T},$$

or

$$\frac{\partial S}{\partial T} = \frac{1}{T}\frac{\partial U}{\partial T}.$$

This expression is indeterminate at the absolute zero, since T and $\frac{\partial U}{\partial T}$ both vanish for $T=0$. It would therefore be quite consistent with thermodynamics that the entropy of a body should become infinite at the absolute zero and have no finite limiting value. We can deduce Nernst's theorem, however, if we assume that the entropy does not become infinite at the absolute zero, but approaches a finite limiting value (which may be zero) as the temperature is lowered.†

Let us consider for this purpose a chemical reaction at the absolute zero. The heat of reaction at constant pressure Q_p is equal to the change in the heat content H of the system consequent on the reaction. The affinity A is equal to the change in the thermodynamic potentials ξ of the reacting substances, *i.e.*

$$Q_p = +\Sigma H \text{ and } A = -\Sigma\xi = -\Sigma H + T\Sigma S.$$

As ΣH and ΣS remain finite at the absolute zero, the affinity A must also remain finite, and hence, by our theorem $\lim_{T=0}\frac{\partial A}{\partial T}=0$. We have therefore

$$\lim_{T=0}\frac{\partial A}{\partial T} = \lim_{T=0}\frac{\partial Q_p}{\partial T} = 0 \text{ (Nernst's theorem).}$$

*On the other hand, if Debye's equation $c_v = \alpha T^3$ is correct at the absolute zero, we should have $\frac{\partial^2 c_v}{\partial T^2} = 6\alpha T$. The second derivative of c_v would then be zero, but its temperature coefficient would not vanish at the absolute zero. (Translator.)

† See Planck, *Thermodynamik*, 3rd edition, p. 268 (1911); also *Berichte d. Deutsch. chem. Gesellschaft*, **45**, 5 (1912).

It follows further, since $\frac{\partial \zeta}{\partial T} = -S$, that

$$\lim_{T=0} \frac{\partial A}{\partial T} = +\lim \Sigma S = 0.$$

In other words, every chemical reaction takes place without change in entropy at the absolute zero. From this it follows that the entropy of a compound is equal to the sum of the atomic entropies. The assumption made by Planck in addition to Nernst's theorem, viz. that the entropy of all substances vanish like the specific heats at the absolute zero, is sufficient but not necessary for the derivation of the heat theorem.

On the other hand, it is a necessary consequence of our hypothesis that the entropy of a body at the absolute zero be independent of the modification or state (solid or supercooled liquid) of the body (Planck).

We have thus shown that Nernst's heat theorem can be deduced from two hypotheses of a very general and plausible character, namely, first that all physical properties which remain finite as the temperature is lowered converge gradually to their limiting value, and, second, that the entropy does not become infinite at the absolute zero, but converges likewise to a finite limiting value.

The author has shown recently * that the second hypothesis can be deduced from the kinetic theory of heat if we accept Einstein's theory that the heat energy in solid bodies is due to vibrations of the atoms whose energy is an integral multiple of a quantum. According to Boltzmann, the entropy of a system containing a large number of atoms is $S = k \log w$, where w is proportional to the ratio of the probability of the state under consideration to the state in which all the atoms are in the same state (*e.g.* in which they all have the same energy of vibration (see p. 158)). At the absolute zero all the atoms are at rest, and therefore in the same state, and hence $w = 1$. The entropy of all substances is therefore zero at the absolute zero (in agreement with the above hypothesis of Planck). The author has also shown (*loc. cit.*) that the entropy increases gradually from

* *Annalen d. Physik*, **34**, 455; see also Jüttner, *Zeitschr. f. Electrochemie*, 17. 139 (1911).

zero to finite values as the temperature is raised; in other words, that S converges gradually to zero as the temperature is lowered.

A solid body whose atoms vibrate with energies which are integral multiples of a quantum, and whose frequency is independent of the temperature and of the specific volume (in accordance with Einstein's theory) possesses at all temperatures some of the properties which we derived on p. 428 for the absolute zero alone. Its coefficient of expansion is zero, and its compressibility is the same at all temperatures (see p. 161). As a body of this kind has very simple properties (analogous to a perfect gas), and as its equation of state can also be deduced from kinetic considerations, we described it by the term " perfect solid body." Real bodies do not conform to these conditions, but the deviations from them appear to diminish at low temperatures. Real solid bodies appear to approach the perfect condition more and more closely as the temperature is lowered. The assumptions made for the perfect solid, *e.g.* independence of the frequency from temperature and volume, are clearly no longer strictly complied with at higher temperatures and greater amplitudes. Real gases deviate likewise from the laws of perfect gases, as these laws are derived from assumptions which hold only at infinite specific volume, *i.e.* at infinite temperature and infinitely low pressure. It is a remarkable fact that we are apparently better acquainted with the molecular state of bodies at very high and very low temperatures than in the intermediate region of temperature which is alone accessible to experimental observation.

APPENDIX.

ENERGY UNITS.

1. *Absolute system.* The unit of work is one erg, *i.e.* the work done by a force of 1 dyne acting for a distance of 1 cm. (see p. 75). 10,000,000 ergs are termed 1 Joule.

2. *Practical system.* The unit of work is one kilogrammeter, *i.e.* the work done by 1 kg. in falling through a height of 1 m.

For our latitudes, 1 kgm. $= 9{\cdot}81 \times 10^7$ ergs.

The work done in one hour at the rate of 75 kgm. per sec. is termed one horse-power hour, *i.e.*

$$1 \text{ horse-power hour} = 75 \times 3600 \text{ kgm.} = 270000 \text{ kgm.}$$

3. *Electrical system.* The electrical unit of work is

$$1 \text{ volt-coulomb} = 1 \text{ watt second} = 1 \text{ Joule} = 10^7 \text{ ergs.}$$

This is the work done by a current of 1 ampere in one second at a potential difference of 1 volt. The technical unit of work is the kilowatt hour, viz.

$$1 \text{ kilowatt hour} = 1000 \times 3600 \text{ watt seconds} = 3{\cdot}6 \times 10^{13} \text{ ergs.}$$

4. *Thermal system.* The unit of heat is the amount of heat necessary to raise 1 gr. of water from 14·5° to 15·5° C. (15° calorie). On p. 79 we found that 1 cal. $= 4{\cdot}19 \times 10^7$ ergs $= 4{\cdot}19$ volt-coulombs. The technical unit is the great calorie :

$$1 \text{ Cal.} = 1000 \text{ cal.} = 4{\cdot}19 \times 10^{10} \text{ ergs} = 427 \text{ kgm.}$$

5. It is often necessary to calculate the work done in the expansion of a gas. The unit of work used here is the litre-atmosphere, *i.e.* the work done when the volume of a gas is increased by 1 litre at a constant pressure of 1 atmosphere. By p. 99, we have

$$1 \text{ litre-atmosphere} = 1{\cdot}01 \times 10^9 \text{ ergs} = 24{\cdot}1 \text{ cal.}$$

Using the above units, we obtain the following figures for the gas constant R :

$$R = 8{\cdot}31 \times 10^7 \text{ ergs}/^\circ \text{C.}$$
$$= 0{\cdot}847 \text{ kgm.}/^\circ \text{C.}$$
$$= 8{\cdot}31 \text{ volt-coulombs}/^\circ \text{C.}$$
$$= 1{\cdot}985 \text{ cal.}/^\circ \text{C.}$$
$$= 0{\cdot}0821 \text{ litre-atmosphere}/^\circ \text{C.}$$

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