

TEXT FLY WITHIN THE BOOK ONLY

*SOME PAGES ARE
MISSING &
DAMAGE BOOK*

UNIVERSAL
LIBRARY

OU₁ 156600

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. *541 N95C* Accession No. *25432*

Author *Noyes, A. A. & Sherrill, W. S.*

Title *Course of study in chemical physics*

This book should be returned on or before the date last marked below.

**A COURSE OF STUDY IN
CHEMICAL PRINCIPLES**



THE MACMILLAN COMPANY
NEW YORK • BOSTON • CHICAGO • DALLAS
ATLANTA • SAN FRANCISCO

MACMILLAN AND CO., LIMITED
LONDON • BOMBAY • CALCUTTA • MADRAS
MELBOURNE

THE MACMILLAN COMPANY
OF CANADA, LIMITED
TORONTO

A COURSE OF STUDY
IN
CHEMICAL PRINCIPLES

BY
ARTHUR A. NOYES
DEPARTMENT PROFESSOR OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
AND
MILES S. SHERRILL
PROFESSOR OF PHYSICAL CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

SECOND EDITION, REWRITTEN

NEW YORK
THE MACMILLAN COMPANY

COPYRIGHT 1922, 1933, and 1934
BY ARTHUR A. NOYES AND MILES S. SHERRILL

COPYRIGHT 1936 and 1938
BY MILES S. SHERRILL

All rights reserved—no part of this book
may be reproduced in any form without
permission in writing from the publisher,
except by a reviewer who wishes to quote
brief passages in connection with a review
written for inclusion in magazine or
newspaper.

FIRST COMPLETE EDITION published May, 1922
SECOND EDITION, rewritten, Parts I and II, published September, 1933;
Part II (continued), November, 1934;
and Part II (concluded), December, 1936
SECOND COMPLETE EDITION published September, 1938

Fourth Printing.

CONTENTS

INTRODUCTION

	PAGE
The Field of Chemistry	1
The Plan of "Chemical Principles"	3

PART I

GENERAL PRINCIPLES RELATING TO MATTER AND ENERGY

CHAPTER I. CHEMICAL SUBSTANCES IN GENERAL

I. THE COMPOSITION AND ATOMIC CONSTITUTION OF SUBSTANCES

	PAGE
1. Matter, Its Measurement and Conservation	9
2. Pure Substances and Mixtures. Elementary and Compound Substances. Elements and Their Conservation.	11
3. Law of Definite Proportions and Law of Combining Weights	13
4. Basic Concepts of the Atomic Theory	14
5. Basic Concepts of the Electronic Theory of the Structure of Atoms	17

II. COMBINING AND ATOMIC WEIGHTS AND CHEMICAL FORMULAS

6. Determination of Combining Weights	21
7. Values of Atomic Weights and Atomic Numbers	23
8. Molecular Weights, Molecular Formulas, and Chemical Formulas in General.	25
9. Expressions of the Chemical Quantities of Substances	27

III. THE PHYSICAL STATES OF SUBSTANCES

10. Physical Properties in General	29
11. Physical Quantities and Units	30
12. States of Aggregation of Substances.	32

	PAGE
13. Factors Determining the Physical Properties of Substances in Any Definite Aggregation-State	32
14. Pressure-Volume-Temperature Relations of Perfect Gases.	34
15. Pressure, Volume, Temperature, or Number of Mols of Gases Evaluated by the Perfect-Gas Equation	37
16. The Components and Phases of Systems	38
17. The Concept of Equilibrium in General.	39
18. Equilibria between the Phases of One-Component Systems	40

CHAPTER II. GENERAL PRINCIPLES RELATING TO THE ENERGY OF SUBSTANCES

I. THE FIRST LAW OF THERMODYNAMICS

1. Energy and Its Conservation. Perpetual Motion of the First Kind	44
2. The First Law of Thermodynamics. System and Surroundings. Heat, Work, and Energy-Content	46
3. Work Attending Processes of Changing the Volume of Systems	50
4. Heat-Effects Attending Processes of Changing the Temperature of Systems. The Concept of Heat-Capacity.	52
5. Heat-Effects Attending Isothermal Processes of Changing the State of Systems	54
6. Increase in Energy-Content Attending Changes in State in General. The Concept of Heat-Content.	56
7. Changes in Heat-Content Attending Changes in the Aggregation-State of Pure Substances at Constant Pressure and Temperature	59
8. Changes in Energy-Content and in Heat-Content Attending Changes in the Temperature of Systems	60
9. Energy-Content and Heat-Content of Perfect Gases	61

II. THE FIRST LAW OF THERMODYNAMICS APPLIED TO THERMOCHEMISTRY

10. Expression of Changes in Heat-Content by Thermochemical Equations.	64
11. Heats of Formation in Relation to Heats of Reaction.	66
12. The Heat of Solution and of Dilution of Substances.	69
13. Heats of Reaction in Aqueous Solution.	71
14. Effect of Temperature on the Heat of Reactions.	73
15. Applications of Thermochemical Principles.	77

VI. SOLUTE-VAPOR-PRESSURE AND SOLUBILITY OF GASES

	PAGE
27. Henry's Law of the Vapor-Pressure of Solutes and of the Solubility of Gases	247
28. Applications of Henry's Law	249
29. Solute-Vapor-Pressure in Relation to Solvent-Vapor-Pressure and to Osmotic Pressure	250

VII. DISTRIBUTION OF SOLUTES BETWEEN PHASES

30. Distribution of a Solute between Two Non-Miscible Solvents	253
31. Applications of the Distribution Law	254
32. Lowering by Solutes of the Solubility of One Solvent in Another Solvent	255

VIII. DEVIATIONS FROM RAOULT'S LAW AT HIGHER CONCENTRATIONS.
PARTIAL VAPOR-PRESSURES IN SOLUTIONS WITH
TWO VOLATILE COMPONENTS

33. Experimental Determination of Partial Vapor-Pressures	256
34. Vapor-Pressure-Composition Diagrams	256
35. Magnitudes of Deviations from Raoult's Law	259
36. Kinetic-Molecular Interpretations of the Deviations from Raoult's Law.	261
37. Other Properties Related to Deviations from Raoult's Law	263

IX. ENERGY RELATIONS OF SOLUTIONS

38. Heat-Content Changes Attending Changes in Volume and Concentration	269
1. Free-Energy Change Attending the Transfer of a Solute between Solutions of Different Concentrations	269
39. Concept of Partial Molar Quantities	272
1. Relation between the Partial Molar Quantities of a Two-Component System	275
2. Relation between the Partial Molar Free Energies and Duhem's Equation	276
3. The Concept of Activity and Its Relation to Molar Free Energy	277
a. States of Reference for Activity	279

MASS-ACTION LAW OF CHEMICAL EQUILIBRIUM AND
ITS THERMODYNAMIC DERIVATION

-Action Law of Chemical Equilibrium	286
Thermodynamic Criteria of Chemical Equilibrium. Derivation of the Mass-Action Law	289

CHAPTER V. THE ELECTRICAL PROPERTIES OF SOLUTIONS AND THE IONIC THEORY

I. MOLAR EFFECTS OF IONIZED SUBSTANCES ON PROPERTIES OF SOLUTIONS. THE IONIC AND ION-ATTRACTION THEORIES

	PAGE
1. Molar Effects of Salts in Aqueous Solutions and Their Explanation by the Ionic Theory	297
2. Ionization of Substances Derived from Their Molar Coefficients	299
3. Basis of the Ion-Attraction Theory	300
4. Molar Coefficients of Salts and Ions Given by the Ion-Attraction Theory	301
5. Molar Effects Derived from the Ion-Attraction Theory of Completely Ionized Solutes on the Properties of Solvents	305
6. Validity of Ion-Attraction Theory in Dilute Solution . . .	306
7. Derivation of the Ion-Attraction Equations	307

II. CHEMICAL CHANGES AT THE ELECTRODES IN ELECTROLYTIC AND VOLTAIC CELLS. FARADAY'S LAW

8. Electrolytic Conduction in General	311
9. Chemical Changes at the Electrodes: Qualitative Effects . .	316
10. Chemical Changes at the Electrodes, Faraday's Law . . .	321
11. The Mechanism of Conductance in Electrolytes	321
12. Expression of the Mechanism of Electrode-Reactions by Electronic Equations	323

III. THE TRANSFERENCE OF IONS

13. Phenomena of Ion Transference and Its Experimental Determination	324
14. Hittorf's Law of Transference	324
15. Transference in Relation to the Mobility of Ions	324
16. Moving-Boundary Method of Determining Transference . .	325
17. Values of Transference-Numbers and Their Variation with Concentration and Temperature	325
18. Composition of Complex Ions Determined by Transference Experiments	325
19. Hydration of Ions Investigated by Transference Measurements	325

IV. ELECTRICAL CONDUCTANCE OF SOLUTIONS

2. The Plan of "Chemical Principles." — The plan of presentation adopted in this book is shown in detail by the Table of Contents. Its main features are here outlined.

In Part I, are presented certain fundamental principles relating to *matter and energy* which underlie both the science of chemistry and the science of physics. First in Chapter I there is briefly reviewed the concepts and laws relating to chemical substances, to their elementary composition and atomic constitution, and to the physical states in which they exist. Then in Chapter II there are discussed in an unusually thorough way the foundations of thermodynamics and the ways in which the laws can be conveniently applied to physicochemical and chemical changes; for upon thermodynamics rests in large measure the modern treatment of theoretical chemistry. Applications of the first law of thermodynamics to thermochemistry are fully treated, applications of the second law, though treated to a limited extent, are taken up in later chapters as the need arises.

In Part II, are developed the *molecular, atomic, and ionic theories* as to the constitution of *substances*; for in the interpretation of chemical phenomena these theories supplement in an important way the laws of thermodynamics and the inductively derived laws of chemistry. These theories are developed, mainly through a consideration of the most directly related physical properties of substances as exhibited in their different states of aggregation, in the following manner.

In Chapter III, are considered the laws regarding the pressure, volume, temperature, and molar composition of gaseous substances, and regarding the energy effects attending changes in these properties; and in connection with these laws the theoretical principles are presented from which molecular weights, atomic weights, and molecular formulas are derived. The molecular kinetic theory of gases is also developed.

In Chapter IV, solutions are treated with respect to those properties whose magnitudes are determined primarily by the number, not by the nature, of the molecules present; and the application of the molecular theory to solutions is considered. In the consideration of the energy relations of solutions, the concept of molar quantities is presented with special emphasis upon molar free energy and its relation to the equilibrium condi-

tions of chemical systems at a definite temperature. The mass action law of chemical equilibrium is derived from the free energy concept, but, as with the second law of thermodynamics in general, its applications are reserved for later chapters as occasion demands.

In Chapter V, solutions are further discussed, especially those of salts, acids, and bases, with respect to their electrical properties; and the ionic theory is developed. The deviations of ionic solutions from the laws of perfect solutes are discussed from the viewpoint of the ion-attraction theory. There is included a thorough thermodynamic treatment of the electromotive force of voltaic cells.

This development of the atomic, molecular, and ionic theories evidently provides a partial treatment of the first major division of the field of chemical principles — the study of the relationships between the physical properties of substances and their chemical composition and molecule-structure. This treatment of these relationships is partial in the respect that it will include only those properties whose interpretation contribute directly and fundamentally to the development of the theories. There are, however, many other physical properties that have important relationships to composition and molecule structure and their consideration would form a large part of a complete presentation of the subject; but this is not included within the scope of this course of study, limited as it is to the more distinctly chemical sides of theoretical chemistry.

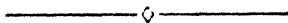
Part III deals with the other major division of chemistry, the field of *chemical changes*. The treatment will be along the general lines of that in the previous edition of "Chemical Principles."

*

In Chapter VI, are considered the laws of the *rates* of chemical changes, and the molecular and kinetic theories of chemical reaction-rate.

In Chapters VII and VIII, the fundamental laws of the *equilibrium* of chemical changes will be presented, mainly from mass-action and phase view-points, but with such use of thermodynamics as is helpful; and these chemical laws, supplemented by the knowledge of the molecular and ionic states of substances previously derived, will be applied to the more important types of chemical reactions.

In Chapter IX, finally, is presented a systematization of the changes in *energy*, *free energy*, and *entropy* attending chemical and physicochemical changes, in relation to their direction and their equilibrium. The third law of thermodynamics is discussed and applied to determine the molar free energy of substances, and hence the equilibrium conditions of chemical systems, from that data alone. The evaluation of the molar entropy, heat-content, and hence free energy of gaseous substances from spectroscopic data is briefly considered.



PART I.

GENERAL PRINCIPLES RELATING TO MATTER AND ENERGY

CHAPTER I

CHEMICAL SUBSTANCES IN GENERAL

I. THE COMPOSITION AND ATOMIC CONSTITUTION OF SUBSTANCES.

1. Matter, Its Measurement and Conservation. — The *quantity of matter* m in a body, also called its *mass* or *weight*, is commonly measured by comparing the gravitational force which acts upon the body with that which at the same place acts upon another body adopted as a standard of reference. The standard body most used for this purpose in scientific work is the prototype *kilogram* (kg.), which is a body made of platinum kept in Sèvres, France. One one-thousandth part of the mass or weight of this standard is adopted as the unit of mass or weight in the so-called absolute centimeter-gram-second (c.g.s.) system of units, which is the fundamental system employed in science. This unit is called the *gram* (g.).

***** The Properties of Mass and Weight and the Concept of Matter.***

The terms mass and weight are discriminatively used to represent the magnitude of the two fundamental properties of bodies which are determined as follows. The *mass* m of a body is determined by the rate at which the body increases its *momentum* mu (where u is its velocity) under the influence of a force f , in accordance with the equation $f = d(mu)/dt$; and the *weight* m of a body (in the sense of its quantity of matter) is determined by the gravitational force f exerted upon the body by the earth (of weight m') at any definite distance l between their centers of gravity, in accordance with the equation $f = j m m' / l^2$, in which j is a universal constant (*Newton, 1686*): it being understood that either of these two effects is compared with that produced upon a body of

**** Throughout the book, as in this instance, a double star is prefixed to the titles of sections or articles, or to paragraphs or problems within articles, which had best be omitted in briefer courses of study, in order that time may be available for topics of more direct importance to the chemist that are treated in later parts of the book. These starred portions of the text are, however, often of much theoretical interest or fundamental significance; and they often serve to make more precise the underlying ideas. They may therefore well be studied by all the students in longer, more thorough courses, or by the abler students in briefer courses.**

standard mass or weight. According to Newton's law of gravitation the mass and weight of bodies are strictly proportional to one another, so that either may be used for the determination of the other.

These properties of bodies, their proportionality to one another, and their conservation (considered below) have led to the concept of an underlying entity called *matter*, of which these properties are manifestations; and to the definition that the *quantity of matter* in a body is proportional either to its mass or to its weight as above defined.

In view of these intimate relationships, quantity of matter may with equal propriety be expressed either by the term mass or by the term weight. And in fact, for this purpose the term mass is commonly employed in the science of physics, since the term weight is there primarily used to denote, not quantity of matter, but a force, namely that between the body and the earth; whereas in chemical writings the term weight is almost always used to denote quantity of matter. This latter practice will be followed in this book, except that mass will be used in kinetic discussions where the inertia of the body is directly under consideration. This difference of usage in physics and chemistry is unfortunate, but can not be avoided without far-reaching changes in the prevailing practices.

Elimination of this divergent usage, however, would not alone suffice to give precision to the three fundamental concepts. This would require the adoption and consistent use of three unambiguous terms, to express respectively:

- (1) The resistance of a body to change in its state of motion (its inertia, or mass as above defined).
- (2) The relative force with which the body and a standard body are attracted to the earth (its weight as above defined).
- (3) The quantity of matter the body contains, whether derived from its mass or weight as above defined.

Of fundamental importance in chemistry and physics is the *law of the conservation of matter*, which states that the mass or weight of any system of bodies remains unchanged, whatever physical or chemical changes take place in it (*Lavoisier, 1777-1789*).

This principle has been tested with great accuracy in the case of chemical reactions (*Landolt, 1893-1910*) by causing them to take place within closed vessels which were weighed before and after the reacting substances were mixed. Thus on mixing within a sealed bulb saturated solutions of barium chloride and sodium sulfate, whereby these substances were converted into

sodium chloride and barium sulfate, it was observed (*Manley, 1913*) that the bulb and contents, which weighed 109 g., varied in weight by less than the average error in weighing, which was 0.006 mg.; showing that this reaction is attended by a change in weight less than one part in ten million.

The *special theory of relativity* (*Einstein, 1905*)* shows, to be sure, that any change ΔE in the energy of a system is attended by a definite change Δm in its mass or weight. This relation is expressed by the following equation, in which c is the velocity of light (2.9977 or approximately 3.00×10^{10} cm. per second):

$$\Delta E = c^2 \cdot \Delta m. \quad (1)$$

It can, however, readily be calculated that even the large evolution of energy that attends some chemical reactions would cause a decrease in the mass of the reacting substances far below the limit of experimental detection. Thus the energy evolution of 94 250 calories which attends the union of 12.0 g. of carbon with 32.0 g. of oxygen to form carbon dioxide is found by Eq. 1 to correspond to a decrease of mass of only 4.4×10^{-6} mg.

2. Pure Substances and Mixtures. Elementary and Compound Substances. Elements and Their Conservation.—Out of the materials occurring in nature there can be prepared substances which, when subjected to suitable processes of *fractionation* (that is, to operations which resolve the materials into parts or fractions), always yield fractions whose properties are

* Names of investigators and the dates of the announcements of their discoveries or experimental researches are inserted throughout this book with two distinct objects in view, as described in the following paragraphs.

(1) Names and dates are attached to the statements of fundamental concepts, laws, hypotheses, or new experimental methods of attack. This is done for historical orientation. The dates indicate in a general way the time when the ideas became effective factors in the development of chemical science, rather than the year when the general ideas may have been first suggested; and the names serve to associate with the ideas the builders of the science. It will be understood that this brief method of reference can not be historically accurate, either in giving due credit to investigators, of whom many often contribute to a single discovery, or in specifying its date, which is often indefinite because a considerable period of time may be required for the development of a new principle.

(2) Names and dates are also attached to statements about experimental investigations, to data cited in confirmation or illustration of principles, and to values of important constants. This serves to indicate the sources of such statements or data and to enable the reader to refer to the original articles, which may be found by consulting abstract journals published in the year mentioned or in the following year.

identical when measured at the same pressure and temperature. Such substances are called *chemical substances*, or better, *pure substances*; other substances which can be resolved by such processes into fractions with different properties being called *mixtures*. For example, whether a solid material is a pure substance or mixture may be determined by partially melting or vaporizing it or by partially dissolving it in solvents, and by comparing the value of the density, melting-point, or some other sensitive property, of the unmelted, unvaporized, or undissolved part with that of the original material.

As another, more specific illustration of this criterion of pure substances consider a sample of gasoline submitted to the following operations (*Washburn, 1930*). The sample was first subjected to systematic fractional distillation, and there were thereby obtained a series of products, each of which boiled at a temperature constant within 0.2° and yielded fractions that showed no detectable differences in density. Such products therefore behaved like pure substances, so far as this process of fractionation indicated. Yet, when certain of them were subjected to fractional freezing, they yielded (solid) fractions which melted at different temperatures. However, by systematic repetition of the freezings separate products were isolated, each of which was not differentiated by further freezings. Any one of these products, not resolvable into fractions of different properties by further freezing, might well be expected to be a pure substance; but it was found that some of these, when subjected again to fractional distillation, were resolved into fractions having different properties. By alternating in this manner systematic distillation with systematic crystallization fractions were finally obtained which could not be further differentiated by either process. To determine whether these products were really pure substances they were subjected to other types of fractionation processes, such as shaking with an immiscible solvent, like aniline or liquid sulfur dioxide; whereby a few of the products were again resolved into distinct fractions. Finally, however, materials were obtained which could not be resolved by any of these processes into fractions of distinguishable properties; and it was therefore considered that pure substances had at last been isolated.

The fundamental idea involved in the preceding considerations is that there exists an order of substances, called pure substances, of relatively great stability toward resolving agencies, each one of which has a perfectly definite set of properties, sharply differentiated from those of other pure substances; so that there is not a continuous series of pure substances whose

properties pass over into one another by insensible gradations. This may be called the *law of definite properties of pure substances*.

Nearly all pure substances, called *compound substances* because of the behavior to be now mentioned, can be converted, by subjecting them to sufficiently powerful resolving conditions, into a small number of other pure substances, called *elementary substances*, which are not further decomposed by chemical or physical processes. In correspondence with this fact all substances are considered to be composed of a small number of kinds of matter called the *elements* (*Boyle, 1661*), each elementary substance consisting of only one of these elements, and each compound substance of two or more of them.

Eighty-nine elements are now well known; but the periodic system and atomic structure considerations suggest that, below uranium, the highest naturally occurring element known, four other elements are capable of existence; and there is experimental evidence which indicates that most of these actually exist on the earth.

Supplementing the law of conservation of matter, there is a *law of conservation of the elements*, which states that the existing quantity of any element is neither increased nor diminished by physical or chemical changes taking place in substances that contain the element.

To this law there are, however, some types of exceptions. Thus the radioactive elements have been found to be undergoing spontaneous disintegration into elements of lower atomic weight; and other elements have been to a small extent artificially transmuted by bombarding their atoms with the swift-moving alpha particles emitted by radio-active substances or with hydrogen-ions given high velocities by an electric field. Nevertheless, the elements constitute a form of matter of an order distinct from that of chemical substances.

3. Law of Definite Proportions and Law of Combining Weights. — The law of definite properties applies also to the elementary composition of pure substances. This fact is expressed by the *law of definite proportions*, which states that a pure substance, whatever its source or however it be prepared, always contains its elements in exactly the same proportions by weight (*Proust, 1799–1808*).

A further law regarding the elementary composition of substances is based upon the fact that to the various elements definite numerical values can be assigned which when multiplied or divided by small whole numbers accurately express the relative weights of the elements which are combined with one another in all pure substances. Such numerical values are called the *combining weights* of the elements; and the corresponding principle is called the *law of combining weights*.

Adopting as a standard of reference 16 as the combining weight of oxygen, the combining weight of any other element may be assigned any value that is equal to the weight of that element which combines with 16 parts of oxygen, or with a quantity of oxygen (such as 8, 24, or 32 parts) which stands to 16 in the ratio of a small whole number. It will be seen from this definition that a combining weight is an arbitrary multiple of an exact quantity.

*Prob. 1. — Combining Weights Arbitrary Multiples of Analytical Values.** — *a.* Two oxides of sulfur are found to contain 50.05% and 40.04% of sulfur. Derive from these analytical results two values for the combining weight of sulfur, and show that these values stand to one another in the ratio of small whole numbers. *b.* Derive a combining weight for iron from the fact that one of its oxides contains 30.06% of oxygen. *c.* Derive two values for the combining weight of iron from the fact that one of its sulfides contains 36.47% of sulfur, for whose combining weight two values were found in *a*; and show that all the values of the combining weight of iron stand to each other in the ratio of small whole numbers. *d.* Arbitrarily representing the first values so found for the combining weights of sulfur and iron by the symbols S and Fe, write chemical formulas for the four compounds analyzed.

Note. — The fact that to these compounds are now always assigned other formulas, namely, SO_2 , SO_3 , Fe_2O_3 , FeS , shows that our whole system of chemical formulas might be highly arbitrary if it had to be based solely upon the gravimetric composition of substances.

4. Basic Concepts of the Atomic Theory. — The fact that elements combine with one another only in the proportions of their combining weights or multiples of them suggested the following *atomic* and *molecular hypotheses* (Dalton, 1803–1808).

* Special attention should always be given to the titles of problems, since the title often shows the problem's broader significance, which may be overlooked in the detailed process of solving it.

(1) The matter constituting each element is made up of extremely small particles, called *atoms*, which are not subdivided by ordinary chemical or physical processes.

(2) The matter constituting chemical substances consists of another order of discrete particles, called *molecules*, which are formed by the association of atoms with one another, usually in small numbers. Elementary substances are composed of molecules consisting of atoms of the same kind, whereas compound substances have molecules consisting of atoms of different kinds.

All the atoms of any definite element were originally thought to be identical in every respect; but many elements have recently been found to exist in two or more forms, called isotopes, whose atoms differ from one another in mass and weight, as well as in certain other respects.

Elementary substances are often loosely spoken of as elements; but this usage should be avoided as it confuses two concepts that are distinct both from empirical and from atomic viewpoints. Thus in the compound lead sulfate the element lead is just as truly present as in the elementary substance metallic lead; and both these substances contain the same kind of lead atoms.

The relative weights of the atoms of the various elements have been determined by many different methods (Part II). The weight of the atom of any element, referred to the weight of the oxygen atom taken as 16, is called the *atomic weight* A of that element.

The relative weights of the molecules of substances that exist in the gaseous and dissolved states have also been determined. The weight of the molecule of any substance referred to the weight of the oxygen molecule taken as 32 (since this molecule has been shown to consist of two oxygen atoms) is called the *molecular weight* M of that substance in the specified state.

It would seem more natural to refer atomic and molecular weights to the atomic weight of hydrogen as unity; and this has been done at times in the development of the system of atomic weights. The oxygen standard has, however, two important advantages. First, in the case of nearly all the elements the values of the combining weights, which underlie the values of the atomic weights, have actually been determined by the analysis of compounds of the elements with oxygen, or with the halogens, whose combining weights have themselves been determined by the analysis of oxygen compounds; so that, if the hydrogen standard were used, it would be necessary to change the whole system of

atomic-weight values whenever a new, more accurate determination of the ratio of the combining weights of hydrogen and oxygen was made. Secondly, many of the atomic weights, among them those of the very important elements carbon, nitrogen, and oxygen, are almost exactly whole numbers on the oxygen standard, but deviate considerably from integers on the hydrogen standard.

The numbers of atoms and molecules contained in definite weights of substances, and therefore also the absolute weights of atoms and molecules, have been recently determined with considerable accuracy. The number of atoms present in even a small quantity of any element and the number of molecules present in even a small quantity of any substance have been found to be enormous; thus, in 1.0078 g. of hydrogen or in one atomic weight in grams of any other element there are contained 6.066×10^{23} atoms; and in 32.00 g. of oxygen gas or in the molecular weight in grams of any other substance there are contained this same number of molecules. Correspondingly, the mass of a single atom or molecule is extremely small; thus that of the hydrogen atom is 0.166×10^{-23} grams.

The adequacy of the atomic and molecular hypotheses has now been confirmed in so many ways that there is no longer any doubt that substances are actually made up of atoms and molecules. These hypotheses have therefore become basic concepts of physical science. By supplementing them by other hypotheses suggested by the observed physical and chemical properties of substances there has been gradually developed (1808–date) a large body of knowledge known as the *atomic and molecular theories*, which include as recent extensions the *ionic theory* as to the state of salts in solutions (1886–date), and the *electronic theories of the structure of atoms and of molecules* (1911–date).

These theories enable the physical properties and chemical reactions of substances to be far more fully correlated and interpreted than would be possible with the aid of inductive generalizations alone. The development and applications of these theories therefore constitute a large part of the study of chemical principles; and to their detailed presentation Part II of this book is devoted. In this chapter, however, there will be immediately considered, first (*I, 5*)*, the basic concepts underlying

* Throughout this book, as in this instance, references to topics considered in earlier or later pages are shown by enclosing within parentheses the number of the chapter in roman numerals followed by the number of the article in arabic numerals. Since chapters and articles are shown in this same way at the inner edge of each page-heading, the reader can readily turn to such references.

ing the electronic and ionic theories, and then (I, 6) the experimental determination of exact values of the combining weights.

5. Basic Concepts of the Electronic Theory of the Structure of Atoms. — The investigations of modern physics have led to the views as to the structure of atoms which are outlined in the following paragraphs.

There exist four elementary entities, known as electrons, positrons, protons, and neutrons. The *electron* (E^-) is a definite quantum of negative electricity, and the *positron*, also called a *positive electron*, is a quantum of positive electricity equal to the negative quantum of the electron. Each of these has a definite mass, probably equal in the two cases. The *proton* H^+ has a mass nearly equal to that of the hydrogen atom, and a charge of positive electricity equal in magnitude to the charge of the electron. The *neutron* has a mass equal or very nearly equal to that of the proton, but has no net charge of electricity.

The magnitudes of these charges and of these masses have been determined by various experimental methods (see below). The electron has been found to have a charge of 1.591×10^{-19} coulomb of negative electricity, and the proton to have an equal charge of positive electricity. These quantities of electricity are often regarded in electronic considerations as unit quantities, which may be called one *electron-charge* e and one *proton-charge*. When at rest and in the free state, the *mass of the electron* has been found to be $1/1838$ of the mass of the hydrogen atom, which is 1.663×10^{-24} gram; and the *mass of the proton* has been found to be less than that of the hydrogen atom by the mass of the electron.

Electrons exist in the free state, separate from other masses, under various conditions; for example, they constitute the cathode rays produced by an electric discharge in an evacuated tube, and the beta rays emitted by radioactive substances. Protons also exist in the free state, for example, in the so-called positive rays produced by an electric discharge through hydrogen gas under special experimental conditions.

Out of electrons and of protons and neutrons the atoms of all the elements are constituted. The atom of hydrogen consists of one proton as a nucleus with one electron remote from it and rotating around it; and the atom of any higher element

consists of a small dense positively charged *nucleus* surrounded by a number of *electrons* at relatively large distances from it (*Rutherford, 1911*), much as the solar system consists of a central sun surrounded by distant planets and satellites.

The size of the nucleus and its distance from the extra-nuclear electrons are indicated by the facts that the helium nucleus has been estimated to have a diameter of 10^{-12} cm. and the helium atom one of 1.9×10^{-8} cm., showing that the extra-nuclear electrons are distant from the helium nucleus by about 20 000 times its diameter.

The nuclei of the atoms of the elements above hydrogen have a positive charge which increases progressively by one proton-charge in the order in which they are arranged in the periodic system; thus it is two proton-charges in the case of helium, three in the case of lithium, four in the case of beryllium, etc., up to ninety-two in the case of uranium (*Moseley, 1913*). Therefore, when expressed in terms of proton-charges, the nuclear charge is equal to the *atomic number* of the element, since this is defined to be its number in the sequence of the elements in the periodic system.

The neutral atom of any element obviously must have a number of electrons outside of the nucleus equal to the number of proton-charges on the nucleus. Moreover, it is to be expected that the charge on the nucleus, since this is a small compact body at a great distance from the extranuclear electrons, will determine primarily the number, location, and motion of these electrons, and that these factors in their turn will determine nearly all the physical and chemical properties of the element. The nuclear charge is therefore the most fundamental characteristic of an atom.

The nuclei of the atoms, except in the case of hydrogen, are now considered to consist of protons and neutrons, intimately associated with one another. This close association is fundamental; for each proton and neutron is an integral part of the compact nucleus, so firmly bound to it that its removal disrupts the atom, whereas (extranuclear) electrons are frequently removed from the atom by physical agencies or transferred to another atom by chemical processes.

From this structure it follows that the mass of the

nucleus is very nearly equal to the mass of the protons and neutrons present, and to the mass of the whole atom; and that the positive charge on the nucleus, expressed in proton-charges, is equal to the number of protons present. Thus, since helium has an atomic weight of about four and an atomic number of two, the helium nucleus consists of two protons and two neutrons; and the neutral helium atom has in addition two (extranuclear) electrons.

Prob. 2. — The Electronic Structure of Atoms. — The element sodium has an atomic number 11 and an atomic weight 23.00. State the number of protons, of neutrons, and of electrons, of which its atom consists.

An atom or atom-group which is electrically charged and is considered to exist as a separate molecule or as an otherwise segregated particle is called an *ion*. From an electronic viewpoint ions arise in two ways, as follows. When from a neutral atom (alone or within a molecule) one or more of its extranuclear electrons are removed there results a positively charged atom or atom-group, which is called a *positive ion*; and when with a neutral atom there are associated one or more electrons from an outside source there results a negatively charged atom or atom-group, which is called a *negative ion*. Thus by removing from the neutral hydrogen atom its electron there results a hydrogen ion H^+ (identical in composition with the proton) with one proton-charge, and by associating with a neutral sulfur atom two electrons there results a sulfur ion (S^{--} or S^-) with two electron-charges; also by a transfer of electrons between the atoms in the molecule of K_2SO_4 there result two positive potassium ions K^+ and a negative sulfate ion (SO_4^{--} or SO_4^-). Ionic considerations are of great importance in interpreting the chemical behavior and physical properties of substances, especially in aqueous solutions, but also in other physical states.

**** *Determination of the Charge of the Electron and the Masses of the Electron and Proton.***

The most precise direct experimental procedure for determining the electron charge e is the oil-drop method (*Millikan, 1908*), which is in principle as follows. Minute drops of oil suspended in air are allowed to fall under the influence of gravity, and the downward velocity u_0 of some one drop, whose mass m_0

is later determined, falling under the gravitational force $m_D g$, is measured by observing with a telescope the time required for it to move through a space corresponding to that between the cross-hairs in the telescope. The drop is then caused (by ionizing the air around it with x-rays) to capture an unknown number n of electrons, whereby it assumes an electric charge $n e$; and it is subjected to an upward-directed electric force $X n e$ by applying between horizontal metal plates above and below the drop a field of known strength X ; and its velocity u is again observed. These two velocities u_0 and u will be proportional to the forces ($m_D g$ and $m_D g - X n e$) acting on the drop in the two cases, since the drop is moving through a medium of large frictional resistance. By formulating this proportionality, there can be determined the value of the ratio $n e/m_D$.

A series of such velocity measurements are made with the same drop after allowing it to take up different unknown numbers of electrons. The separate values of $n e/m_D$ calculated from these measurements are found to stand to one another in the ratio of small whole numbers, thus establishing the fundamental principle that electric charges are taken up in the form of multiples of a definite quantum of electricity. Provided enough experiments are made, it is almost certain that in some of them only one electron will have become attached to the drop; so that the smallest observed value of $n e/m_D$ will be the value of e/m_D ; or, if this is not the case, the greatest common divisor of all the observed values will be so.

In order to determine the mass m_D of the drop, its radius r is calculated from the viscosity η of the air and the velocity u_0 with which the drop falls through it under the influence of the force of gravity f , by means of Stokes' law, — a principle of mechanics which is expressed by the equation $f = 6 \pi r \eta u_0$. The mass of the oil-drop is calculated from the so-found radius, and from the density of the oil, thus giving all the data needed for finding the electron-charge e .

The masses of the electron and of the proton have been obtained from this value of the electron-charge by combining it with values of the ratio e/m of the charge to the mass for the electron and for the proton. The values of this ratio have been determined by measuring the angular deflection which streams of electrons or of protons undergo when they pass through electric and through magnetic fields. This deflection depends also on the velocity of the particles; but the velocity factor can be eliminated by combining the separate effects produced by an electric field and by a magnetic field.

This deflection method of determining the charge-mass ratio is applicable to streaming electrified particles of any kind, thus to the alpha and beta particles emitted by radioactive substances; and it has been much used in developing electronic theories.

II. COMBINING AND ATOMIC WEIGHTS AND CHEMICAL FORMULAS.

****6. Determination of Combining Weights.**—The atomic theory evidently requires that the weights of elements that combine with one another be proportional to the weights of their atoms or to multiples of those weights; in other words, that the atomic weights be equal to the combining weights or stand to them in the ratio of whole numbers. The determination of the exact atomic weight of an element therefore involves:

(1) Determination of its combining weight by quantitative analysis or synthesis of some of its compounds.

(2) Determination of that multiple or submultiple of its combining weight which is its atomic weight.

Methods of determining combining weights will be now described. The principles by which the multiples which are the atomic weights have been established are considered in Part II.

The combining weight of an element is experimentally determined by preparing one of its compounds or the elementary substance itself in a state of the highest possible purity, and completely converting it into another pure substance, the other elements contained in the substances being of known combining weights. The quantities of the initial substance taken and of the final substance obtained are accurately weighed, and from the ratio of these weights the combining weight is calculated. For example, the combining weight of hydrogen has been determined by converting hydrogen gas into water with the following results.

In a series of eleven experiments (*Morley, 1895*) the total quantity of hydrogen burned was 40.9178 g., of oxygen consumed was 324.8684 g., and of water formed was 365.7836 g. The combining weight of hydrogen (referred to oxygen as 16.0000) derived from the weight-ratio of hydrogen to oxygen is 2.01523 or 1.00761, and from the weight-ratio of oxygen to water is 2.01510 or 1.00755. These results evidently show that the atomic weight of hydrogen is 2.0152 or some multiple or submultiple of this number. If the molecule of water consisted of one atom of hydrogen and one of oxygen, as was for a long time assumed, the atomic weight of hydrogen would be 2.0152; since, however, the molecule is now known to consist of two atoms of hydrogen and one of oxygen, the atomic weight of hydrogen, as derived from these data, is 1.0076.

It is noteworthy that this important combining-weight ratio, because it involved the exact weighing of gases and the obtaining of pure hydrogen, was accurately determined only late in the history of combining-weight determinations. Thus previous to the publication (in 1895) of the above-cited results the atomic weight of hydrogen was considered to be 1.0025, thus to have a value 0.5% smaller than the present value 1.0081.

Some of the other exact determinations of combining weights on which the present system of atomic weights is based are the following. From a series of extensive researches made with unusually large quantities of carefully purified substances (*Stas, 1860-1865*) precise values were first derived for the combining weights of some of the most important elements (Probs. 3, 4); namely, of silver, potassium, sodium, lithium, lead, chlorine, bromine, iodine, sulfur, and nitrogen. The following comparison of some of the atomic weights so obtained with those now accepted shows the remarkable degree of accuracy of this early work.

	<i>Silver</i>	<i>Potassium</i>	<i>Sodium</i>	<i>Chlorine</i>	<i>Bromine</i>	<i>Iodine</i>	<i>Sulfur</i>
Stas, 1865	107.938	39.136	23.057	35.453	79.963	126.86	32.06
Present	107.880	39.096	22.997	35.457	79.916	126.92	32.06

The exact combining weights of other elements were later determined by a variety of methods, of which the most common (Prob. 5) is the analysis of the pure chlorides or bromides of the elements by precipitation of the halogen as its silver salt (*Richards, Baxter, Hönigschmid, 1894-date*).

**** Typical Methods of Determining Combining Weights.**

Prob. 3. — Combining Weights of Silver, Potassium, and Chlorine. — a. In a series of eight experiments a total of 801.48 g. of carefully purified potassium chlorate, when ignited or treated with hydrochloric acid, yielded oxygen and 487.66 g. of potassium chloride. Show from these data that the precise value for a combining weight of potassium chloride is 24.862. *b.* In another series of five experiments 24.452 g. of purified potassium chloride were dissolved in water and precipitated with silver nitrate, whereby 47.013 g. of silver chloride were obtained; the ratio of which numbers, here given to lessen the numerical work, is 1.9226. And in a third series of ten experiments 82.669 g. of silver, dissolved in nitric acid and precipitated with hydrochloric acid, yielded 109.840 g. of silver chloride (the ratio of these two weights

by not more than a few units. Several other elements are known to exist, but the values of their atomic weights are very uncertain.

The table shows also the *atomic numbers*, which denote the sequence of the elements in the periodic system, and which have a special significance in relation to the electronic structure of the atoms (I, 5).

8. Molecular Weights, Molecular Formulas, and Chemical Formulas in General. — The molecular weight of a substance in the gaseous state or in the dissolved state can be derived with the aid of certain theoretical principles from measurements of suitable physical properties of the gas or solution. From the molecular weight of the substance so determined, from the relative quantities of the various elements it contains, and from the atomic weights of these elements there can then be very simply determined the number and kinds of atoms of which the molecule consists. The so-determined composition of the molecules of any substance is expressed by its *molecular formula*, in which the symbols of the elements are now considered to represent single atoms and are written in sequence with appropriate subscripts; thus the molecular formula of ethyl ether is $C_4H_{10}O$. Molecular formulas express also the gravimetric composition of substances, since the symbols of the elements are considered to represent not only their atoms, but also their (relative) atomic weights.

The molecular weights and molecular formulas of substances in the pure liquid state are much less fully and less reliably known than in the gaseous or dissolved states, and those in the crystalline state are often inherently indefinite. There is therefore usually assigned to a substance in either of these aggregation-states a *chemical formula* which expresses the elementary composition of the substance and the relative numbers of the atoms of the different elements present, but does not show what multiple of the simplest possible formula represents the molecules that are actually present in those aggregation-states. In case the liquid or crystalline substance can be vaporized and its molecular weight in the gaseous state has been determined, its chemical formula is usually made identical with its molecular formula in the gaseous state. In case the liquid or crystalline substance can not be vaporized without decomposition, the simplest chem-

ical formula is assigned which will represent the relative number of atoms that are present. Thus it is usual to represent liquid acetic acid and liquid nitric acid by the formulas $C_2H_4O_2$ and HNO_3 , which are the molecular formulas of gaseous acetic acid and of gaseous nitric acid; and to represent manganese dioxide and starch by the formulas MnO_2 and $C_6H_{10}O_5$, which are the simplest formulas which express the elementary composition and relative numbers of atoms present. It is to be borne in mind, however, that such chemical formulas do not necessarily represent the weight or composition of the molecules of the substance in the liquid, solid, or dissolved state. Thus acetic acid in the liquid state probably consists mainly of $C_4H_8O_4$ molecules; and nitric acid in dilute aqueous solution exists mainly as the ions H^+ and NO_3^- , not as HNO_3 molecules.

A further complication, especially common in the liquid or dissolved state, is that some substances, judged to be pure substances by the criterion that upon fractionation they yield fractions of identical properties (1, 2), sometimes contain more than one kind of molecule. It is therefore often desirable to employ a term to represent a substance which contains only a single kind of molecule. Such a substance is called a *chemical species* or *molecular species*. Pure substances, to be sure, are normally single chemical species; but they may consist of two or more chemical species which are capable of conversion into one another, and which are always present in definite proportions at any given temperature and pressure in consequence of the very rapid establishment of equilibrium between them. Thus, water-vapor at small pressures is a pure substance which consists only of a single chemical species with molecules of the form H_2O ; but liquid water is also a pure substance, although it contains several chemical species, with molecules such as H_2O , H_4O_2 , H_6O_3 , since these are always present in definite proportions at any given temperature and pressure, because equilibrium is almost instantaneously established between them.

Pure substances which, like water, water-vapor, and ice, are converted into one another by changes of pressure and temperature are commonly spoken of as the same substance; but they may consist of different chemical species, as has just been illustrated.

9. Expressions of the Chemical Quantities of Substances. — In order to express the quantities of substances in ways convenient in chemical considerations, conventions are in use which correlate the quantities with the atomic or molecular weights of the substances, and with their chemical formulas.

Under these conventions the symbol of the element is considered to represent, besides its atom and its (relative) atomic weight, that number of grams of the element which is equal to its atomic weight; and this number of grams is called one *atomic weight* (1 atwt.), or sometimes one gram-atomic weight or one gram-atom. Correspondingly, the chemical formula of an elementary or compound substance is considered to represent the weight in grams which is equal to the sum of all the weights represented by the symbols of the elements and their subscripts in the formula. This weight is called one *formular weight* (1 fwt.) of the substance. Thus the formula HNO_3 denotes $1.008 + 14.008 + (3 \times 16.000)$ or 63.016 grams of nitric acid.

Just as one formular weight of a substance is defined as the number of grams of it corresponding to its chemical formula, so one *molecular weight* or one *molar weight* of a substance is defined as the number of grams of it which is equal to its molecular weight as expressed by its molecular formula. This quantity of a substance, which is sometimes called also one gram-molecular weight or one gram-molecule, is more briefly designated *one mol* — the term which will be used throughout this book. The relation of mols to formular weights corresponds to the relation between molecular formulas and chemical formulas which has already been discussed (I, 8). Thus when it is desired to show only the quantity of substance, considered without special reference to its molecular state, this quantity, sometimes called the *stoichiometric* quantity, is appropriately expressed by specifying the number N_f of formular weights corresponding to a specified formula; but when, as often in theoretical considerations, it is desired to show the quantity of a particular chemical species, this quantity should be expressed by specifying the number N of mols corresponding to the molecular formula of that species.

Those weights of various substances which are the quantities that enter into chemical reactions with one another are said to be *equivalent*. Adopting one atomic weight or 1.0081

grams of the element hydrogen as the standard of reference, the *equivalent-weight* or *one equivalent* of any substance is defined to be that weight of it which reacts with this standard weight of hydrogen, or with that weight of any other substance which itself reacts with this standard weight of hydrogen. Thus the equivalent-weight of each of the following substances is that fraction of its formular weight which is indicated by the coefficient preceding the formula: $\frac{1}{2}\text{Cl}_2$; $\frac{1}{4}\text{O}_2$; 1Ag ; $\frac{1}{2}\text{Zn}$; $\frac{1}{3}\text{Bi}$; 1NaOH ; $\frac{1}{2}\text{Ba}(\text{OH})_2$; $\frac{1}{2}\text{H}_2\text{SO}_4$; $\frac{1}{3}\text{H}_3\text{PO}_4$; $\frac{1}{3}\text{AlCl}_3$; $\frac{1}{4}\text{K}_4\text{Fe}(\text{CN})_6$. The quantity of a substance in a system under consideration may evidently be expressed by stating the number N_{eq} of equivalents present.

The equivalent-weight of a substance may have different values, called its *metathetic equivalent* and its *oxidation-equivalent* respectively, depending on whether the substance is considered with reference to a reaction of metathesis or to one of oxidation and reduction. Thus, the metathetic equivalent of ferric chloride is $\frac{1}{3}\text{FeCl}_3$, but its oxidation-equivalent (with respect to its conversion to ferrous chloride) is 1FeCl_3 ; and the metathetic equivalent of potassium chlorate is 1KClO_3 , but its oxidation-equivalent (with reference to its reduction to KCl) is $\frac{1}{6}\text{KClO}_3$. The magnitude of the oxidation-equivalent may be ambiguous unless the product resulting from the reduction of the substance is specified.

III. THE PHYSICAL STATES OF SUBSTANCES.

10. Physical Properties in General.—The physical properties of substances may be classified as extensive and intensive. An *extensive property* is one whose value is dependent not only on the nature of the substance and the conditions under which it exists, but also is proportional to the quantity of it under consideration. Thus the volume v and heat-capacity C of liquid water at 20° and 1 atm. are obviously extensive properties, since their values are proportional to the weight considered. An *intensive property* is one whose value under definite conditions of pressure and temperature is characteristic of the substance, either because it is inherently independent of the quantity present or because it is defined with reference to a specified quantity. Thus inherently intensive properties of the substance liquid water at 20° and 1 atm. are its refractive index, its viscosity, and its vapor-pressure; and intensive properties referred to definite quantities of water are its specific volume or specific heat-capacity.

From the value of the extensive property of any quantity of a substance there can always be derived a value for the corresponding intensive property by referring the value to one gram or to one formula weight or one molecular weight of the substance. The value of a property that is possessed by one gram of a substance is called the *specific value* of that property, and is denoted in this book by a straight line placed above the general symbol of the property; and the value of a property that is possessed by one formula weight or by one mol of the substance is called its *formula* or *molar value*, and is here denoted by a wavy line placed above the symbol of the property. For example, in the case of any pure substance at a definite temperature and pressure, the symbol $\bar{v}$ (read v bar) represents its *specific volume* (equal to v/m), and the symbol $\bar{C}$ represents its *specific heat-capacity* (equal to C/m). Similarly, the symbol $\tilde{v}$ (read v formula or molar) represents its *formula* or *molar volume*, and the symbol $\tilde{C}$, its *formula* or *molar heat-capacity*.

The term *specific* is appropriately applied also to values of a property which are referred to unit-values of determining factors other than weight, such as volume, length, or cross-section; thus specific gravity denotes the weight of one milliliter, and specific resistance denotes the resistance of a centimeter cube.

The term specific was formerly used to denote the ratio of the value of the specified property of the substance to that of an equal weight or volume of water; and this use still continues to some extent; especially in the terms specific heat and specific gravity. It seems desirable, however, that the term specific be used only in the sense stated above.

11. Physical Quantities and Units. — Some of the more important physical quantities and units employed in physico-chemical considerations, and the symbols by which they are represented in this book are the following.

Mass or weight m : gram (g.); milligram (mg.).

Length l : centimeter (cm.); millimeter (mm.); micron (μ); angstrom ($\text{\AA}$).*

Time t : second (sec.); minute (min.); hour (hr.).

Velocity u (equal to dl/dt): centimeter per second (cm./sec.).

Area a : square centimeter (sqcm.).

Volume v : liter (l.); milliter (ml.) or cubic centimeter (ccm.).†

Density $\bar{m}$ (equal to m/v): gram per milliter (g./ml.).

Concentration c (equal to N/v): mol per liter (molal, m.)‡;

c_f (equal to N_f/v): fwt. per liter (formal, f.);

c_{eq} (equal to N_{eq}/v): equivalent per liter (normal, n.).

Force f : dyne.

Pressure p (equal to f/a): bar (dyne/sqcm.); millimeter of mercury (mm.); atmosphere (atm.).

Energy E : erg; joule (j.); calorie (cal.).

Temperature on the ordinary scale t or t° : centigrade degree ($^\circ\text{C}$ or simply $^\circ$).**

Temperature on the absolute scale T : centigrade degree ($^\circ\text{A}$).

Potential v , or electromotive force E : volt.

Quantity of electricity Q : coulomb; faraday (F coulombs); electron-charge e .

* One micron (abbreviation for micro-meter) is 10^{-6} meter or 10^{-4} cm. One angstrom is 10^{-8} cm.

† One milliter is defined to be the volume of one gram of pure water at the temperature of its maximum density under a pressure of one atmosphere. One cubic centimeter is the volume of a cube with an edge one centimeter in length. 1 ml. equals 1.000 027 ccm.

‡ Concentration in the case of solutions is expressed also in various other ways (IV , J).

** Time and ordinary temperature are here both represented by t ; but when confusion would arise, t° is used to denote ordinary temperature. The value of the temperature is understood to be on the ordinary centigrade scale, unless the letter A is affixed to the degree sign to indicate that the value is on the absolute scale. Many physicists use K for this last purpose.

With respect to the concepts and units of force, pressure, temperature, and energy, the following definitions may be recalled.

(1) A *force* f is measured by the rate at which it increases the *momentum* (mu) of a body upon which it acts; that is, $f = d(mu)/dt$.

(2) *One dyne*, the centimeter-gram-second (c.g.s.) unit of force, is the force which acting on a freely moving mass of one gram increases its velocity each second by one centimeter per second.

(3) The *force of gravity* acting on a mass of one gram at any place is g dynes; and the standard value g is 980.665 (980),* which is equal within 0.01% to that prevailing at sea-level in a latitude of 45°.

(4) *One atmosphere* is defined to be equal to 1.01325×10^6 dynes per square centimeter (approximately 1.013 megabars). It is equal within 0.01% to the pressure exerted by a column of mercury 760 mm. in height at 0° at sea-level in a latitude of 45°, where its density is 13.595 (13.60).

(5) *One erg* is equal to the work attending the displacement of a force of one dyne through one centimeter (in correspondence with the equation $E = fl$); or it is equal to the kinetic energy possessed by a mass of two grams moving with a velocity of one centimeter per second (in correspondence with the equation $E = \frac{1}{2} m u^2$). *One joule* is 10^7 ergs.

(6) *One calorie* (1 cal.), as used in this book, is equal to the heat required to raise the temperature of one gram of water from 15° to 16° under the pressure of one atmosphere. One calorie is equal to 4.185 (4.18) joules; this value being the so-called *mechanical equivalent of heat*. This calorie is equal within 0.03% to the *mean calorie*, which is one hundredth of the heat required to raise the temperature of one gram of water from 0° to 100°.

(7) *One centigrade degree* is the temperature-difference which produces in the product ($p v$) of the pressure and volume of a perfect gas one one-hundredth part of that product's fractional increase which results when the gas is heated from the temperature (0° C) of (air-saturated) water freezing, to that (100° C) of water boiling at one atmosphere pressure. Temperature expressed on the absolute scale ($I, 14$) in centigrade degrees is 273.16° (273°) greater than that expressed on the ordinary scale.

* Here and throughout the book bold-face type is used to show the approximate values of fundamental constants which it is well to remember. To the exact values in ordinary type are often appended these rounded-off values in bold type. These approximate values are always given with an accuracy of 0.10-0.25 percent, and may be used in all problems where precision is not specified. Also the symbols of fundamental constants are set in bold-face italic type, as in the cases of e and g in the above list, whenever they might otherwise be confused with casual values of the same physical quantity or with some other physical quantity.

12. States of Aggregation of Substances. — The physical properties of substances vary greatly with their states of aggregation, and the physico-chemical generalizations relating to properties are therefore naturally considered, as in Part II of this book, in connection with these states.

The *aggregation states* in which pure substances commonly exist are the *gaseous state* (perfect or imperfect), the *liquid state*, the *solid crystalline state* (metallic or nonmetallic), and the *solid amorphous state*. Important in the case of mixtures of substances are also the *dissolved state* or *state of solution*, in which the substances form physically homogeneous mixtures containing aggregates no larger than molecules, and the *dispersed state* where a substance, called the *colloid*, is disseminated in the form of small aggregates of molecules throughout a gaseous, liquid, or solid medium.

To show the aggregation-state of a substance in physico-chemical considerations there is often appended to its formula the letter (g) for gaseous, (l) for liquid, and (s) for solid. The number of mols or formular weights considered is also shown by prefixing a symbol or number to the formula. Thus $N \text{ Cl}_2(\text{g})$ denotes N mols of gaseous chlorine; $1 \text{ H}_2\text{O}(\text{l})$, one formular weight of liquid water; and $0.2 \text{ KCl}(\text{s})$, 0.2 formular weight of solid potassium chloride. When solid substances exist in two or more crystalline forms, the one that is under consideration is shown by adding its common name or that of its crystalline state to the formula; for example, 1 C (diamond) , or $1 \text{ CaCO}_3 \text{ (rhombic)}$.

13. Factors Determining the Physical Properties of Substances in Any Definite Aggregation-State. — In order to fix the values of all the physical properties of a specified quantity of a pure substance (or of a mixture of specified composition) which exists in any definite single aggregation-state, it is necessary and sufficient to specify the values of two determining factors, such as the pressure and temperature. For example, the value of any property, such as the specific volume $\bar{v}$ or specific energy-content $\bar{E}$, of water (or of a 30% mixture of water and alcohol) that exists in the liquid state is fully determined when and only when the values of its pressure and temperature (or of some other two variables) are specified, thus when the water (or mixture) is stated to be at one atmosphere and 20° . This principle is

expressed in functional notation by equations such as $\bar{v} = f(p, T)$, or $\bar{E} = f(p, T)$.

Of importance is the definite form of the function $v = f(p, T)$ that expresses under specified conditions the relation between the volume of a pure substance (or type of substance) and the pressure and temperature. This definite function is called the *equation of state* of the substance (or type of substance).

An equation of state is almost always limited to a definite aggregation-state, and usually to a specified range of pressure and temperature, or even to a specified pressure or specified temperature. Thus the equation of state of any gaseous substance at very small pressure is $p\bar{v}/T = R$, where R is a constant having the same value for all substances; and the equation of state of a liquid substance at any specified temperature and through the range of pressure within which the compression-coefficient β can be considered constant is $v = v_0(1 - \beta p)$, where v_0 is the volume of the liquid at zero pressure, and β varies with the nature of the substance and its temperature.

The equation of state of gases at very small pressures will be considered in detail here (I, 14), since the pressure-volume-temperature relations of such gases have fundamental significance with reference to the concepts of absolute temperature and of molecular weight, and with reference to the development of the laws of thermodynamics. The equations of state of substances under other physical conditions will be considered later, as occasion requires.

Functional Notation and Partial-Derivative Notation.

Whenever the value of a property of a substance or mixture of substances is fully determined by specifying the values of only two determining factors (two independent variables) as in the above cited instance, or in general, by specifying the values only of some definite number of determining factors, this may be expressed in two ways: either briefly and qualitatively, by using functional notation, such as the expression $\bar{v} = f(p, T)$ which signifies that to determine the specific volume of the substance it *suffices* to specify the pressure and temperature; or more specifically, by employing partial-derivative notation as follows:

$$dv = \left(\frac{\partial v}{\partial p}\right)_T dp + \left(\frac{\partial v}{\partial T}\right)_p dT. \quad (2)$$

Partial-derivative notation is in this book employed to only a limited extent. It is used mainly as a clear short-hand expression of physical concepts and principles and as a simple means of deriving relations between the changes in a property that depends on two independent variables.

To those not familiar with partial derivatives the following statement and problem will make clear the notation and usage.

In the above equation (Eq. 2) relating to volume changes the *partial derivative* $\left(\frac{\partial v}{\partial p}\right)_T$ (read partial of v with respect to p , T constant) denotes the rate of increase of the volume v with the pressure p when the temperature is kept constant at T ; and the whole term $\left(\frac{\partial v}{\partial p}\right)_T dp$ therefore represents the absolute increment of volume produced by a change dp in the pressure when the temperature is kept constant. Correspondingly, the partial derivative $\left(\frac{\partial v}{\partial T}\right)_p$ denotes the rate of increase of the volume with the temperature T when the pressure is kept constant at p ; and $\left(\frac{\partial v}{\partial T}\right)_p dT$ therefore represents the absolute increment in volume produced by a change dT in the temperature when the pressure is kept constant. And the equation as a whole states that the total volume-increment dv producible by any infinitesimal changes whatever in the determining factors (here by the changes dp and dT) is the sum of all the volume-increments (expressed here by the last two terms of Eq. 2) which result when each of these factors is separately varied.

Prob. 6. — Pressure-Increase Attending the Heating of a Liquid at Constant Volume Derived from the Partial Differential Equation. — a. Derive from Eq. 2 an expression for $(\partial p/\partial T)_v$. *b.* For ethyl alcohol at 20° and 1 atm. 0.000105 is the fractional decrease in volume per atmosphere (called the *isothermal compression-coefficient* β), and 0.00108 is the fractional increase in volume per degree (called the *thermal expansion-coefficient* α). Calculate from the differential equation derived in *a* the increase in pressure that would keep the volume constant when alcohol at 1 atm. is heated from 20 to 22° , assuming the coefficients to be constant through the small range of pressure and temperature involved. *Ans.* 20.6 atm.

14. Pressure-Volume-Temperature Relations of Perfect Gases. — As the pressure of a gaseous substance approaches zero, it approaches the state of a *perfect gas*, and it conforms to certain principles known as the *laws of perfect gases*. These laws express

the relations between the volume v of the gas, the pressure p and absolute temperature T to which it is subjected, and the number N of mols of which it consists. These relations are given by the following expression, which is the equation of state for a perfect gas, and which is called briefly the *perfect-gas equation*:

$$pv = NRT. \quad (3)$$

In this equation R is a *universal constant*, that is, one not dependent on the nature of the substance involved. It is known as the *gas-constant*, and is evidently equal to the value of pv/T for one mol of any perfect gas.

Prob. 7. — Evaluation of the Gas-Constant. — From the fact that one gram of oxygen (formula O_2) has a volume of 7004 ml. at 0° and 0.1 atm., under which conditions oxygen deviates only very slightly from the perfect-gas laws, calculate a precise value of the gas-constant R , a , when the pressure is in atmospheres and the volume in milliliters; b , when the pressure-volume product is in calories. (For exact values of the constants needed see I, 11.)
Ans. a, 82.06.

The values of the gas-constant R when the pressure-volume product is expressed in various units are shown in Table II. In energy considerations this gas-constant is often expressed in joules or calories per degree per mol, even though the value then has no simple relation to the usual units of pressure and volume.

TABLE II. VALUES OF THE GAS CONSTANT.

<i>Pressure in</i>	<i>Volume in</i>	<i>Pressure-Volume Product in</i>	<i>Gas-Constant</i>
Atmospheres	Milliliters	Ml.-Atm.	82.05 (82)
Atmospheres	Liters	Liter-Atm.	0.08205
Dynes per sqcm.	Ccm.	Ergs	8.314×10^7
....		Joules	8.314
....		Calories	1.9866 (1.99)

The perfect-gas equation rests upon two experimentally established laws; but it involves also two definitions, that of absolute temperature and of number of mols. One of these laws is *Boyle's law*, which states that at any definite temperature the

volume of any definite quantity of any definite perfect gas is inversely proportional to its pressure, or that the density of any definite perfect gas is proportional to its pressure (*Boyle, 1660*). The other law is *Gay-Lussac's law of temperature effect* (also called *Charles' law*), which states that different perfect gases undergo the same fractional increase in their pressure-volume product when heated from the same initial to the same final temperature (*Gay-Lussac, 1802*); thus an increase of 36.61% occurs in the pressure-volume product of all perfect gases when heated from the temperature of ice melting under a pressure of one atmosphere to the temperature of water boiling under this pressure.

The proportionality, expressed by the perfect-gas equation, between the pressure-volume product of a perfect gas and the absolute temperature is, however, only secondarily a consequence of Gay-Lussac's law. This proportionality rests primarily on the definitions that *temperature-difference* is proportional to the change it produces in the pressure-volume product of a perfect gas (*I, 11*), and that *absolute temperature* is proportional to the pressure-volume product itself. These definitions have been adopted because they lead to simple expressions of the laws of perfect gases and of the second law of thermodynamics.

Since on the ordinary centigrade scale the temperatures of melting ice (in contact with air-saturated water) and boiling water at one atmosphere are taken as 0° and 100° , the increase of 36.61% which the heating from 0° to 100° causes in the pressure-volume product shows that these temperatures are 273.16° and 373.16° on the absolute centigrade scale, and therefore that in general $T = t + 273.16$.

The perfect-gas equation evidently involves another quantity, the mol, which has been in a formal way defined to be the number of grams in one molecular weight of the substance, but for which no experimental method of determination has yet been described. The equation, to be sure, if supplemented by the theoretical principle known as Avogadro's law, affords a simple and direct means of determining molecular weights (*III, 1, 2*); but for the expression of the pressure-volume-temperature relations of gases (here under consideration) and for the thermodynamic applications of these relations (*II, 21, 22*) a purely empirical definition suffices, which may be stated as follows.

One mol (or *one molar weight*) of any gaseous substance is the number of grams of it which in the state of a perfect gas has the same value of $p v/T$ as do 32.00 grams of oxygen when in the state of a perfect gas. This arbitrary standard of reference is adopted, since oxygen as 16.00 has been taken as the standard of reference for atomic weights (*I*, 4), and since the molecule of oxygen has been found to consist of two atoms (*III*, 3). Of practical importance is, furthermore, the fact that *one mol* of a gaseous or vaporizable substance is in general the number of grams corresponding to its chemical formula, since this is usually so written as to represent its molecule in the gaseous state (*I*, 8).

15. Pressure, Volume, Temperature, or Number of Mols of Gases Evaluated by the Perfect-Gas Equation. — In the case of a gas at small pressure any one of the properties named in the title can be approximately evaluated with the aid of the perfect-gas equation; for obviously this equation enables any one of the four variables p , v , T , N occurring in it to be calculated when the other three are known. Moreover, for this purpose it is ordinarily preferable to use this equation, rather than to follow the plan, often employed in elementary instruction, of setting up proportions involving the molar gas volume under so-called standard conditions (thus 22.413 l. at 0° and 1 atm.). As an aid in quickly estimating gas volumes, however, it is well to note that at one atmosphere the molar volume of a perfect gas at T° is $82 T$ ml. (within 0.1%), and at 20° is 24 l. (within 0.2%).

Although air is a mixture, it has in different localities a fairly constant composition (*III*, 7), and at small pressures it conforms to the laws of Boyle and Gay-Lussac. The pressure-volume-temperature relations of air at small pressures can therefore be simply computed with the aid of the perfect-gas equation by regarding air as a single substance and considering it to have a molar weight equal to the number of grams which have the same value of $p v/T$ as 32 grams of oxygen. The so-defined molar weight of air is computed from the most accurate density determinations to be 28.98 (29).

Properties Evaluated by the Perfect-Gas Equation.

Prob. 8. — Calculate precisely the volume of one mol of a perfect gas, a , at 0° and 1 atm.; b , at 20° and 1 atm. *Ans.* a , 22 413 ml.; b , 24 054 ml.

Prob. 9. — Calculate the volume of 12 g. of the vapor of ethyl ether ($C_4H_{10}O$) at 80° and 60 mm.

Prob. 10. — *a.* Calculate the number of mols that are contained in 7 g. of a gaseous substance whose volume is 6.35 l. at 20° and 720 mm. *b.* Calculate the molecular weight of the substance.

Prob. 11. — Calculate the molar weight of pure dry air from the fact that its density is 0.001293 at 0° and 1 atm.

Note. — In the problems throughout the book, unless precision is asked for, gases at pressures not exceeding one atmosphere may be assumed to conform to the perfect-gas equation, and the round value of the gas-constant, 82 milliliter-atmospheres per degree, may be used. As stated previously, approximate values (accurate within 0.1–0.2%) of fundamental constants, which it is well to remember and which may be used in problems not demanding precision, are printed in bold-face type.

16. The Components and Phases of Systems. — The definite kinds and quantities of substances that are under consideration are said to constitute the *system*.

Any pure substances (*I*, 2) which suffice to produce the system under all the equilibrium conditions under consideration are called the *components* of the system; and in correspondence with the minimum number of pure substances which so suffice, the system is said to be one-component, two-component, etc. For example, a system consisting of liquid water, ice, and water-vapor is a one-component system; for it can be produced by taking a single pure substance, water. And a system consisting of solid ammonium chloride and its aqueous solution is a two-component system, even though it contains a large number of chemical species (NH_4Cl , NH_4^+ , Cl^- , HCl , NH_3 , NH_4OH , H_2O , H_4O_2 , etc.); for it can be produced by taking two pure substances, namely, solid ammonium chloride and liquid water.

A system, whether it consists of one component or several components, may be physically homogeneous throughout its extent, or it may consist of two or more parts, each physically homogeneous but differing from the other parts in properties and separated from them by definite boundaries. Such physically homogeneous parts are called the *phases* of the system; and in correspondence with the number of them existing under the specified conditions the system is said to be one-phase, two-phase, etc. Systems with only one phase are often called *homogeneous systems*; and those with two or more phases, *heterogeneous systems*. The term homogeneous from an experimental view-point

signifies that there can not be detected in any way a difference in physical properties throughout the extent of the phase, and from a molecular view-point it implies that there are present no larger aggregates than the molecules themselves.

Systems never have more than one gaseous phase, since all gases are miscible; but systems often have two liquid phases, and may have several crystalline phases. For example, systems composed of bromine and water may form at room temperature, besides a gaseous phase containing the vapors of the two substances, two liquid phases, one composed of much bromine and little water, and the other of much water and little bromine; and at lower temperatures solid phases may appear consisting of pure bromine, pure ice, or the pure hydrate $\text{Br}_2 \cdot 10\text{H}_2\text{O}$. So also, systems composed of sodium sulfate and water may form at different temperatures, in addition to a gaseous phase and a solution, solid phases consisting of ice, Na_2SO_4 , $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, or $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

17. The Concept of Equilibrium in General. — In the study of chemical principles there are few concepts more fundamental than that of equilibrium. In general, a system is said to be in *equilibrium* under specified conditions when under those conditions no change can take place in the system.

In cases where the processes by which the equilibrium may be approached occur at a measurable rate, one can determine whether or not equilibrium has been established:

(1) By finding whether the density, composition, or other property of any phase of the system undergoes change after a sufficiently long interval of time.

(2) By finding whether the system assumes the given state, characterized by definite properties, when it is caused to approach this state from the two opposite sides.

For example, at 25° liquid water is in equilibrium with its vapor when this vapor has a pressure of 23.8 mm. This is shown by the fact that the liquid does not vaporize nor the vapor liquefy, however long they are kept in contact at 25° ; and further by the facts that if water is put into contact in one experiment with its vapor at 17.5 mm. at 20° , and in another experiment with its vapor at 31.8 mm. at 30° , and the two

systems are then brought to 25°, the pressure of the vapor soon assumes in both cases the identical value of 23.8 mm.

In cases where the processes of approaching equilibrium are very slow, or where the substances are so inert that the equilibrium will never be directly attained, it may be doubtful whether or not a given state is one of equilibrium; and in such cases the fact that a detectable change is not taking place must not lead to the mistaken conclusion that the change can not take place, and that therefore the system is in equilibrium. For example, a mixture of hydrogen and oxygen gases at room temperature does not produce a detectable quantity of water in a year; yet that the gases are not in a state of equilibrium is shown by the fact that they are rapidly converted almost completely into water when placed in contact with metallic palladium. Also diamond exists in nature through geologic ages without being converted into graphite; yet the latter is shown by thermodynamic considerations to be the equilibrium state of carbon at ordinary temperatures and pressures.

18. Equilibria between the Phases of One-Component Systems. — A general *law of phase equilibrium* is that the absolute quantities of the various phases of a system do not influence the composition of the phases. As examples may be cited the facts that the composition of a solution in equilibrium with a solid salt is not dependent on the quantity of the solid in contact with the solution; that the pressure or composition of the vapor in equilibrium with a definite liquid solution is not dependent on the quantities of liquid and vapor in contact with one another; and that the proportions of hydrogen and water-vapor in a gaseous phase in equilibrium with solid iron and solid ferrous oxide are not dependent on the quantities of these solid phases in contact with the gaseous phase. — The rate at which equilibrium is established between phases is, however, greatly increased by increasing the extent of the surfaces between them.

The conditions of equilibrium are simplest in one-component systems — those whose phases can all be produced out of a single pure substance, such as water. Thus it has already been seen (*I, 13*) that, when such a system exists in a single phase, all its intensive properties, such as its specific volume or density, refractive index, and viscosity, become definite when

and only when two determining factors, commonly its temperature and pressure, are specified. Hence at a definite temperature the substance may have any pressure, and at a definite pressure it may have any temperature (within the range within which the phase exists).

Two phases, however, of a one-component system can exist in equilibrium with each other only at one definite pressure when the temperature is specified, or at one definite temperature when the pressure is specified. Thus at 25° liquid water and water-vapor coexist in equilibrium only when the pressure is 23.8 mm.; and at a pressure of one atmosphere they coexist in equilibrium only at 100° . And at 0° ice and water are in equilibrium only when the pressure is one atmosphere; and at 590 atmospheres they are in equilibrium only when the temperature is -5.00° . In other words, inasmuch as the equilibrium pressure is determined when the temperature is fixed, or the equilibrium temperature is determined when the pressure is fixed, any intensive property of either of the phases of a one-component two-phase system becomes definite when either the pressure or the temperature is specified. Thus for the specific volume of either phase, $\bar{v} = f(p)$ or $\bar{v} = f(T)$, instead of $\bar{v} = f(p, T)$ as in a one-phase system.

When a liquid or solid phase is present with a gaseous phase, the equilibrium-pressure is called the *vapor-pressure* of the liquid or solid at the specified temperature; the equilibrium temperature is called the *boiling-point* of the liquid at the specified pressure; and the gaseous phase is said to consist of *saturated vapor*. When a solid phase is present with a liquid phase, the equilibrium temperature is called the *melting-point* of the solid, or the *freezing-point* of the liquid, under the specified pressure. When two solid phases (like the two crystalline forms, rhombic sulfur and monoclinic sulfur) are present together, the equilibrium temperature is called the *transition-point* at the specified pressure, and the equilibrium pressure is called the *transition-pressure* at the specified temperature. — When the pressure is not stated, it is understood, in the case of a melting-point, boiling-point, or transition-point, to be one atmosphere.

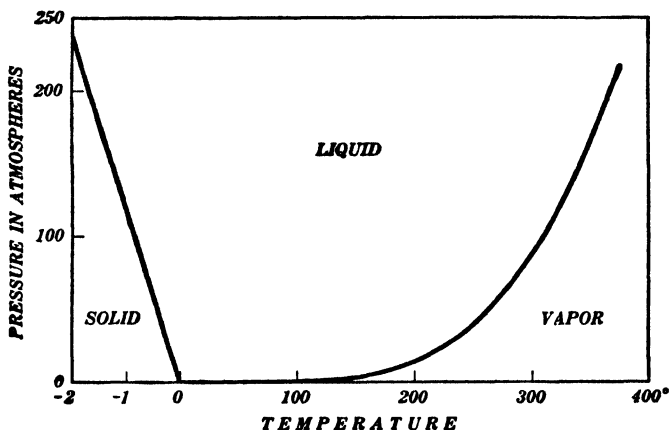
Three phases of a one-component system can coexist in equilibrium only at one definite pressure and temperature; thus,

ice, liquid water, and water-vapor are in equilibrium only at 4.6 mm. and 0.0098° . At this temperature and pressure all the properties of all three phases are fully determined. The temperature at which three phases of any one-component system are in equilibrium is called the *triple-point*.

The number of determining factors (independent variables) whose values can and must be specified in order to fix the intensive properties of each phase of a system that is in a state of equilibrium is called the *variance* of the system. Thus a one-component system that exists in a single phase is *bivariant*; one that exists in two phases is *univariant*; and one that exists in three phases is *nonvariant*.

The experimentally determined equilibrium conditions of one-component systems are clearly represented by *pressure-temperature diagrams*. Figure 1 is a diagram of this kind, which represents the behavior of water at temperatures above -2° , different scales being used for the temperatures above 0° and for those below 0° . The three areas show the range of temperatures and pressures within which water exists as a single, solid, liquid, or gaseous phase. The left-hand graph is a melting-point curve showing the temperatures and pressures at which ice and liquid water coexist in equilibrium; and the right-hand graph is a vapor-pressure curve showing the temperatures and pressures at which liquid water and water-vapor coexist in equilibrium.

FIGURE 1. PRESSURE-TEMPERATURE DIAGRAM FOR WATER.



This graph ends at 374° and 218 atm., which for water are the *critical temperature* and *critical pressure*, at which the liquid and gaseous phases become identical and above which the substance never resolves itself into two phases.

The conditions of equilibrium between the phases of systems consisting of more than one component are considered in later chapters.

Prob. 12. — Interpretation of Pressure-Temperature Diagrams of One-Component Systems. — With the aid of Fig. 1 determine approximately: *a*, the freezing-point of water at 50 atm., and the mean change of its freezing-point per atmosphere; *b*, the vapor-pressure of water at 250° ; *c*, the boiling-point of water at 80 atm.; *d*, the state in which the substance water exists when its pressure is 50 atm. and its temperature 200° ; *e, f*, the changes in phase that take place in the substance water initially at 50 atm. and 200° , *e*, when its temperature is gradually decreased to -1° , and *f*, when its pressure is gradually decreased to 1 atm. *g*, Describe a process by which liquid water at 50 atm. and 200° could be changed to vapor at 50 atm. and 400° without at any time becoming heterogeneous.



CHAPTER II

GENERAL PRINCIPLES RELATING TO THE ENERGY OF SUBSTANCES

I. THE FIRST LAW OF THERMODYNAMICS.

1. Energy and Its Conservation. Perpetual Motion of the First Kind. — Energy manifests itself in a variety of forms, but in its general aspects it may be defined by the statement that *energy* is heat or anything that is transformable into heat; *heat* being understood to be that which passes between bodies when they are at different temperatures. Correspondingly, the *quantity of energy* existing in any form other than heat may be determined by measuring the quantity of heat which that energy is capable of producing, thus by measuring the rise in temperature which that heat causes in a known weight of some standard substance, such as water. The units in which in scientific treatments energy is commonly expressed have already been defined (*I, 11*).

The essential idea underlying the concept of energy (*Mayer, 1842; Joule, 1845; Helmholtz, 1847*) is that there exists an entity, involved in all the changes taking place in the universe, whose total quantity always remains unchanged. This is often explicitly expressed by the statement that energy is neither created nor destroyed in any process whatever. This statement, called the *law of the conservation of energy*, is stated more concretely as follows: When a quantity of energy appears or disappears at any place, a precisely equal quantity of energy simultaneously disappears or appears at some other place or places; and when a quantity of energy appears or disappears in any form, a precisely equal quantity of energy simultaneously disappears or appears in some other form or forms; equal quantities of energy of different forms being understood to be those quantities which when converted into heat produce the same quantities of heat.

The exactness of this law has been established by many careful quantitative investigations made for the purpose. The law is also confirmed by the correspondence of the conclusions drawn from it with well-established facts and principles. Among

these may be mentioned the following principle, based upon the failure of many attempts to produce a contrary result: The production of energy in the form of work by an arrangement of matter (by a machine) which itself undergoes no permanent change and which withdraws no energy from the surroundings is an impossibility. The result of an ideal process of this kind, by which an unlimited quantity of work could be produced out of nothing, is sometimes called *perpetual motion of the first kind* — to distinguish it from another kind of perpetual motion later described (II, 10). Incidentally it may be noticed that *perpetual motion* is a conventional term which really means production of work in unlimited quantity by a machine which itself undergoes no permanent change.

The Concepts of Energy and Force.

In the historical development of the science of mechanics, the concept of force (*Newton, 1686*) was introduced long before that of energy (*1842–1847*). For Newton's so-called *first and second laws of motion* are in effect qualitative and quantitative definitions of force; thus the first law defines force as that which causes change in the state of motion of bodies, and the second law specifies that the magnitude of a force f be measured by the rate at which it changes the *momentum* mu of a body upon which it acts; that is, $f = d(mu)/dt$, where m is the mass of the body and u is its velocity-component in the direction in which the force acts. The work dW involved when a body is displaced under the influence of a force f through a distance dl was later defined by the equation $dW = f dl$; and by combining the equations $f = m du/dt$ and $dW = f dl$, the work involved in accelerating a body was seen to be expressed by the equation $dW = m u du = d(\frac{1}{2}mu^2)$. When later these types of work were recognized as forms of energy, the corresponding energy equations $dE = f dl$ and $dE = d(\frac{1}{2}mu^2)$ were formulated.

This historical development is still commonly followed in the elementary presentation of these fundamental concepts. It has, however, the disadvantage that it makes force the primary concept and makes energy, though far more fundamental, a secondary concept. A systematic treatment based upon energy is readily obtained by proceeding in the converse manner, as follows. Define quantity of energy to be equivalent to the quantity of heat it can produce. Express kinetic energy by the equation $E = \frac{1}{2} m u^2$, in virtue of the experimental fact that the quantity of heat produced when the kinetic energy of a moving body is transformed into heat is proportional to the mass of the body and

to the square of its velocity. Define force primarily in terms of energy by the equation $f = dE/dl$; and show by combination of these two equations that the Newtonian concept of force $f = m du/dt$ follows as a secondary definition.

As a consequence of the above-outlined historical development, in elementary textbooks energy is still often defined as the power of doing work (instead of producing heat). This definition is an unfortunate one, since it is the essence of the second law of thermodynamics (II, 10) that heat, which is a form of energy, can not be quantitatively converted into work, though work can always be quantitatively converted into heat.

2. The First Law of Thermodynamics. System and Surroundings. Heat, Work, and Energy-Content. — Of great importance in chemical considerations are the energy effects attending changes in the state of systems. By the *system* (I, 16) is understood the definite kinds and quantities of matter arbitrarily taken under consideration. A system is said to be in a definite *state* when all of its properties are definite; and this is the case when there are specified the temperature and pressure and a limited number of the properties of the system, such as the state of aggregation, quantity, and chemical composition of each of its phases. A change in any of these conditions is called a *change in state* of the system. Thus the system under consideration might consist of 16 grams of the element oxygen and 2.0162 grams of the element hydrogen. This system might exist initially in the state of a mixture of oxygen gas ($\frac{1}{2}\text{O}_2$, g) and of hydrogen gas (1H_2 , g) at a temperature of 20° and a pressure of ten atmospheres; and it might then undergo a change in state, and exist finally in the state of liquid water ($1\text{H}_2\text{O}$, l) at 1 atm. and 20° .

It follows from the impossibility of perpetual motion of the first kind that, when the state of a system is fixed, the quantity of energy associated with the system, which is called its *energy-content* E , is also fixed. In other words, energy-content is a property fully determined by the state of the system, and hence any specified change in its state is attended by a definite change in its energy-content, whatever be the *process* by which the change takes place. This principle, applicable to any property, is called the *law of initial and final states*.

This corollary from the law of the conservation of energy is of great importance in chemical and physical considerations. As an example, consider one gram of ice at 0° to be converted

into saturated water-vapor at 0° , first by subliming the ice directly, and secondly by melting the ice and then vaporizing the water. Since the same change in state is brought about by two different processes, the change in the energy-content of the system must be equal for the two processes; that is, the energy absorbed from the surroundings in subliming the ice must be equal to the sum of the energies absorbed in melting the ice and vaporizing the water.

Any change in the energy-content of the *system* must, of course, be attended by an equivalent energy effect in the *surroundings*; and in fact the change in the energy-content of a system is almost always determined by measuring the energy imparted to or withdrawn from the surroundings.

The energy lost or gained by the system may appear or disappear in the surroundings in any of its various forms; but in energy considerations it is primarily important only to differentiate the production of *heat* from that of the other forms of energy. Such other forms of energy which may be associated with matter are collectively designated *work*. All these forms of work are quantitatively transformable into one another, but the transformation of heat into work is subject to certain limitations, which will be considered later; and it is for this reason that heat and work are differentiated from each other. The branch of science which deals with the relations between heat, work, energy-content, and work-producing power is called *thermodynamics*.

Some of the *forms of energy* included under the term *work* are the energy which a body has in virtue of its motion (called its *kinetic energy*), or in virtue of its position with respect to other masses (called its *gravitational energy*), or in virtue of its tendency to undergo increase in volume against a pressure (called its *compression energy*); or the energy which an electric charge has in virtue of its position with respect to other charges or in virtue of its electric potential (called its *electrostatic energy*); or the energy which a system has in virtue of its tendency to undergo chemical changes (called its *chemical energy*).

With the aid of the concepts of energy-content, heat, and work, and of system and surroundings, the law of the conservation of energy may now be expressed by the statement that when a definite system undergoes a change from some specified

(initial) state (State 1) to some other specified (final) state (State 2) the increase ($E_2 - E_1$) in the energy-content of the system is equal to the heat Q absorbed from the surroundings diminished by the work W produced in them. That is,

$$E_2 - E_1 = Q - W. \quad (1)$$

Or, for any definite infinitesimal change in state,

$$dE = dQ - dW. \quad (2)$$

The law of conservation of energy is called the *first law of thermodynamics*. Its expression in either of these forms is known as the *first-law equation*. Of the quantities involved in the first-law equation the increase in energy-content is most fundamental, since it has a definite value for any definite change in state; whereas the relative quantities of heat and of work involved may vary with the *process* by which the change in state takes place.

Thermodynamic Significance of the Terms Work and Heat.

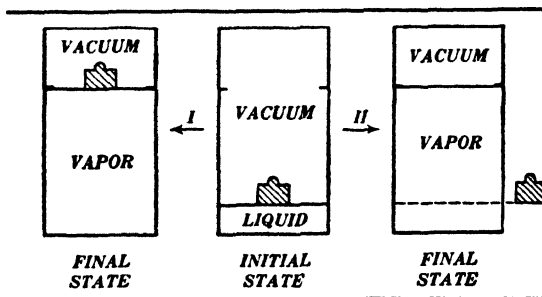
It is to be noted that the term work is used in thermodynamics in a different sense from that in which it is used in mechanics, where it denotes the displacement of a force through a distance whether or not this results in a change in the work or in the work-producing power of the surroundings. For example, when a gas expands and raises a weighted piston, work in a thermodynamic sense is produced in the surroundings equal to the increased energy possessed by the weight in virtue of its higher level, whereas in a mechanical sense work is said to be done also in overcoming the force due to friction; but, inasmuch as this does not increase the work-producing power of the surroundings, it is not regarded as thermodynamic work. In this book work is always used in its thermodynamic sense, and is said to appear or disappear in the surroundings, or to be produced or destroyed in the surroundings. The expression *work done* upon or by the system is to be avoided, since it is apt to lead to confusion.

Also the term heat is used in thermodynamics in a purely empirical sense — thus without the molecular implications often attached to it in general physics. Namely, it denotes simply that kind of energy, whatever its intrinsic nature, which when transferred from or to the surroundings causes in them a change (infinitesimal or finite) in their temperature; and it is used without reference to any form of energy, such as the energy due to the translational motions of the molecules, from which this power of producing temperature changes may be assumed to arise.

It is also to be noted that, unlike the quantity dE , the quantities dQ and dW occurring in Eq. 2, though infinitesimal, are not differentials of a property determined by the state of the system. Correspondingly, though Q and W in Eq. 1 represent finite quantities of heat withdrawn from and of work produced in the surroundings, such as might result from the summation of the infinitesimal heat and work quantities dQ and dW attending a finite change in state brought about by infinitesimal steps, yet these quantities Q and W are not integrals of any function of the state of the system. Therefore, these quantities would not appropriately be represented by $Q_2 - Q_1$ and $W_2 - W_1$, since the subscripts 2 and 1 are used in thermodynamic expressions in this book to denote properties of the final and initial states of a system.

To show more fully the significance of the first-law equation, two different processes (I and II) of bringing about the same change in state and the application to these processes of the first-law equation are illustrated by Fig. 1 and by the description which follows it.

FIGURE 1. TWO PROCESSES OF BRINGING ABOUT THE SAME CHANGE IN STATE.



System: one gram of water, in a cylinder with a weightless frictionless piston, with a vacuum above the piston.

Initial state (State 1): liquid at 100° and 1 atm.

Final state (State 2): vapor at 100° and 1 atm.

Surroundings: a large heat-reservoir at 100° , and a weight which placed on the piston produces a pressure of 1 atm.

Process I: The weight on the piston is decreased^a by an infinitesimal amount, and the piston rises till all the water vaporizes.

Heat Q_1 withdrawn from the surroundings (the reservoir) 540 cal.

Work W_1 produced in the surroundings (weight raised to higher level)..... 40 cal.

Energy-content increase $E_2 - E_1$ of the system. .500 cal.

Process II: The weight is removed from the piston, and the piston rises till all the water vaporizes.

Heat Q_{II} withdrawn from the surroundings (the reservoir).....	500 cal.
Work W_{II} produced in the surroundings (no weight raised)	0 cal.
Energy-content increase $E_f - E_i$ of the system. .	500 cal.

The foregoing considerations show that, in order to evaluate the change in energy-content attending a definite change in the state of a system, it is necessary to determine the quantities of work produced in the surroundings and of heat withdrawn from or imparted to the surroundings by some process by which that change in state is brought about. The determination of the work effects and of the heat effects in the surroundings that attend certain important types of processes are next considered (II, 3-5); after which the corresponding changes in energy-content are discussed (II, 6-9).

3. Work Attending Processes of Changing the Volume of Systems. — The work produced when a system changes its volume against an externally applied pressure is of especial importance in chemical considerations. Work so produced (whether positive or negative) will be called *expansion work*.

Expansion work is most readily derived for the case that the volume undergoes a change in dimensions in one direction only. Consider that a liquid or gaseous substance is contained in a vertical cylinder closed by a movable piston of area a , and that a force f is exerted upon this piston, for example, by a weight placed upon it. Suppose that the piston rises through a distance dl . By the familiar definition of mechanics the work dW produced is $f dl$, and the applied force acting downward upon the surface of the piston is the product $a p_{ap}$ of its area a into the applied pressure p_{ap} . The product $a dl$ of the distance into the area is, however, the increase in volume dv . The work dW produced by the expansion against the applied pressure is therefore given by the equation:

$$dW = p_{ap} dv. \quad (3)$$

It can easily be demonstrated that this equation holds true also in the case that the volume changes in any number of directions. The equation is therefore a general one.

In thermodynamics the expansion is almost always considered to take place against an applied pressure p_{ap} which is made substantially equal to the pressure p exerted by the system itself. In this case the work dW produced by the expansion is given by the expression

$$dW = p \, dv. \quad (4)$$

That is, the work produced in the surroundings when a system undergoes an infinitesimal change in volume against an externally applied pressure that is substantially equal to the pressure of the system itself is the product of that pressure into the increment of volume.

By the *work* W attending a change in volume of a system will hereafter be understood, unless otherwise stated, the work produced when the applied pressure is equal to the pressure p exerted by the system. The work so produced is called the *maximum work* of expansion; for obviously it is the largest quantity of work that can conceivably be produced by the process of expansion, since the process would not occur if the applied pressure were greater than the pressure of the system.

The two limiting cases, where the applied pressure is substantially equal to the pressure of the system and where the applied pressure is zero, are exemplified by the two processes of vaporizing a liquid illustrated by Fig. 1 (II, 2), which produce respectively the maximum work and no work whatever.

The maximum work attending a finite change from an initial volume v_i to a final volume v_f is given by the integral

$$W = \int_{v_i}^{v_f} p \, dv. \quad (5)$$

To carry out this integration there must be known the function which expresses the relation between the pressure and volume of the system throughout the volume interval involved in the process.

For the two simplest types of processes, those attended by no change in volume and by no change in pressure, Eq. 5 obviously becomes:

$$W = 0, \text{ for a process at constant volume.} \quad (6)$$

$$W = p(v_f - v_i), \text{ for a process at constant pressure.} \quad (7)$$

For the maximum work produced by the change of N mols of a perfect gas from volume v_1 and pressure p_1 to volume v_2 and pressure p_2 at a constant temperature T , Eq. 5, when combined with the perfect-gas equation (I, 14), gives the following expressions, in which, as always in this book, $\ln$ denotes natural logarithm:

$$W = N R T \ln \frac{v_2}{v_1} = N R T \ln \frac{p_1}{p_2}. \quad (8)$$

Maximum Work Attending Various Physical Changes in State.

Prob. 1. — Vaporization of a Pure Substance at Constant Temperature and Pressure. — *a.* Calculate the work in ergs and in calories (I, 11) that is produced when one formular weight of liquid water (1 H₂O, 1) vaporizes at 100° against an applied pressure of 1 atm., which is equal to the pressure of its saturated vapor (I, 18) at 100°. At 100° and 1 atm. the specific volume of liquid water is 1.043 ml., and that of saturated water-vapor is 1677 ml. *b, c.* Find the percentage error that would be made, *b*, by neglecting the volume of the liquid; *c*, by regarding the vapor as a perfect gas (I, 14). *d.* Show that under the approximate assumptions of *b* and *c* the work produced by the vaporization at a constant temperature T of that quantity of a liquid which forms N mols of saturated vapor is approximately given by the expression $W = N R T$.

Prob. 2. — Fusion of a Pure Substance at Constant Temperature and Pressure. — Calculate the work in calories attending the fusion of one formular weight of ice under a pressure of 1 atm. at its melting-point 0°, where its density is 0.917 and that of water is 1.000. (Note that this work is very small in comparison with that found in Prob. 1a, where a gas was involved.)

Prob. 3. — Expansion of a Perfect Gas at Constant Temperature. — *a.* Derive from Eq. 5 the expressions (Eqs. 8) for the maximum work that attends at temperature T the change of N mols of a perfect gas from pressure p_1 and volume v_1 to pressure p_2 and volume v_2 . *b.* Calculate the work in calories produced when at 20° one mol of a perfect gas expands till its volume is doubled. *Ans. b,* 404 cal.

Prob. 4. — Heating of a Perfect Gas at Constant Pressure. — With the aid of the perfect-gas equation show that the maximum work produced when N mols of a perfect gas are heated one degree at constant pressure is $N R$ ergs or calories.

4. Heat-Effects Attending Processes of Changing the Temperature of Systems. The Concept of Heat-Capacity. —

The ratio of the quantity of heat dQ absorbed by a system from the surroundings when the temperature of a system rises from T to $T + dT$ to the rise of temperature dT is called its *heat-capacity* C (often, inappropriately, its specific heat); that is, $C = dQ/dT$. The heat-capacity is substantially equal to the quantity of heat absorbed when the temperature rises one degree. When the heating takes place without change of pressure, the heat absorbed per degree is called the *heat-capacity at constant pressure* C_p . When the heating takes place without change of volume, the heat absorbed per degree is called the *heat-capacity at constant volume* C_v . That is,

$$C_p = \frac{(dQ)_p}{dT} \quad (9); \quad C_v = \frac{(dQ)_v}{dT} \quad (10).$$

The heat-capacity of any homogeneous system is obviously the product of its weight by the heat-capacity of one gram of it, which last is called its *specific heat-capacity* $\bar{C}$. The heat-capacity of one mol or one formula weight of a pure substance is called its *molar* or *formula heat-capacity* $\tilde{C}$. The heat-capacity of one atomic weight A of an elementary substance is called its *atomic heat-capacity* $A \bar{C}$. When not otherwise stated, any of these heat-capacities is understood to be at a constant pressure of one atmosphere.

Prob. 5. — Heat-Capacity Concepts Illustrated by a Method of Determining the Heat-Capacities of Gases. — Hydrogen was allowed to flow at a constant rate under a pressure of one atmosphere past an electric heater within a tube which was surrounded by an evacuated vessel to prevent loss of heat. Electrical energy was supplied to the heater at a known rate. When a steady state was reached, the grams of gas flowing per second, the joules of electrical energy supplied per second, and the rise in the temperature of the gas were for three temperatures of the entering gas those shown in the following table.

<i>Temperature of Entering Gas</i>	<i>Grams of Gas per Second</i>	<i>Joules per Second</i>	<i>Rise in Temperature</i>
15.5°	0.001413	0.12312	6.110°
— 78.	0.001937	0.09215	3.612
— 183.	0.001259	0.04357	3.122

Calculate the molar heat-capacity at constant pressure of hydrogen in calories per degree at each of the three temperatures, noting that 1 cal. is 4.185 joules (I, 11).

The heats dQ and Q absorbed in changing the temperature of a system from T to $T + dT$ or from T_1 to T_2 are evidently given in terms of its heat-capacity C by the expressions:

$$dQ = C dT; \quad \text{or} \quad Q = \int_{T_1}^{T_2} C dT. \quad (11)$$

In order to carry out the integration, the heat-capacity C is commonly expressed as an empirical function of the absolute temperature, such as the following in which C_0 , C' , C'' , . . . are experimentally determined constants:

$$C = C_0 + C' T; \quad \text{or} \quad C = C_0 + C' T + C'' T^2, \dots \quad (12)$$

Prob. 6. — Heat-Effect Attending Change in Temperature in Terms of Heat-Capacity. — a. Formulate an expression for the heat absorbed in heating from T_1 to T_2 at constant pressure N mols of a substance whose molar heat-capacity $\bar{C}_p$ is expressed by a function like that of Eq. 12. *b.* Calculate the calories evolved when one gram of nitrogen is cooled at 1 atm. from 600° to 20° ; its molar heat-capacity within this temperature range being $6.732 + 2.88 \times 10^{-4} T + 5.3 \times 10^{-8} T^2$. *Ans. b,* 143 cal.

5. Heat-Effects Attending Isothermal Processes of Changing the State of Systems. — Processes taking place at a constant temperature are called *isothermal processes*. The simplest of these are those that take place without change in volume or without change in pressure. The quantities of heat absorbed by such processes are called respectively the *heat at constant volume* Q_v and the *heat at constant pressure* Q_p .

These two types of heat-effect are illustrated by the heats of vaporization involved in the two vaporization processes previously considered (Fig. 1; II, 2), and by the heats of reactions considered below (Prob. 8; II, 6).

The heat-effect at constant pressure (and temperature) is the one which is most commonly measured and recorded in tables, whether the process is a physical change or a chemical reaction. This heat-effect is usually experimentally determined, not by a single direct measurement, but by measuring the heat-effects that attend a two-step process which results in the same change in state as the direct isothermal process. Both steps of this two-step process take place under a constant pressure, such as that of the atmosphere. The first step is, in principle, an *adiabatic process*, that is, one taking place without interchange of

heat between the system and its surroundings. In this step there is brought about a change in state similar to the isothermal one under consideration, but differing from it in the respect that the system in its final state is not at the initial temperature, but is at the higher or lower temperature which results when the process is adiabatic (instead of isothermal). In the second step the system is restored to its initial temperature by the addition or withdrawal of a quantity of heat. The change in temperature in the first step is accurately measured; and the heat added or withdrawn in the second step is evaluated, either by direct measurement or by multiplying the change in temperature by the (known) heat-capacities of the substances and solutions present. Since the same change in state results from this two-step process and from the one-step isothermal process, the two processes must be attended by the same change in energy-content. But in this case the two processes must be attended also by the same heat-effect, inasmuch as they produce the same quantity of work, namely, $p(v_2 - v_1)$. This is true of the work produced since all the changes are carried out under the same (constant) pressure p , and since the final and initial volumes v_2 and v_1 of the system are the same in the two processes.

Prob. 7. — Experimental Determination of the Heat-Effects Attending Isothermal Changes in State. — a. Consider a system consisting of a calorimeter containing 50 H_2O (l) and 1 KCl (s). In the initial state the water and salt are separate, and the temperature of the calorimeter and its contents is 20.00° . Then the water and salt are mixed, and the temperature falls to 15.11° (this being the value obtained after correcting the observed reading to adiabatic conditions by taking into account the rate at which the calorimeter actually takes up heat from the surroundings). Consider now that the system is heated to 20.00° ; and calculate the heat that must be absorbed to produce this result from the facts that the heat-capacity of the calorimeter itself is 19 cal. per degree and that the specific heat-capacity of the solution of 1 KCl in 50 H_2O is 0.904 cal. per degree. (This quantity of heat is evidently equal to the heat absorbed by the dissolving of 1 KCl (s) in 50 H_2O (l) at 20.00° (the initial temperature), a quantity which may be called the formular heat of solution of potassium chloride in 50 fwt. of water at 20.00° .) *b.* Outline such a modification of the two-step process described above as would enable the heat of solution at 15.11° (the final temperature) to be calculated from the same calorimetric measurement. *c.* Calculate its value, noting that the specific heat-capacity of potassium chloride is 0.166.

6. Increase in Energy-Content Attending Changes in State in General. The Concept of Heat-Content. — The first law of thermodynamics (II, 2) shows that the increase in the energy-content attending any definite change in the state of a system may be found by considering some process by which that change in state is brought about, and by subtracting from the heat withdrawn from the surroundings the work produced in them by that process. When the process, whether or not attended by a change in temperature, produces no work other than expansion work the first-law equations evidently become:

$$dE = dQ - p dv. \quad (13); \quad E_2 - E_1 = Q - \int_{v_1}^{v_2} p dv. \quad (14)$$

$$E_2 - E_1 = Q_v, \quad \text{for a process at constant volume.} \quad (15)$$

$$E_2 - E_1 = Q_p - p(v_2 - v_1), \quad \left\{ \begin{array}{l} \text{for a process at} \\ \text{constant pressure.} \end{array} \right\} \quad (16)$$

Prob. 8. — Energy-Content Changes and Heat-Effects of Reactions at Constant Pressure and at Constant Volume. — A mixture of 0.2 mol of CO and 0.1 mol of O₂ at 20° and 1 atm. is converted into CO₂ at 20° by two different processes. In one case this is done at a constant pressure of 1 atm. (by burning the mixture within a calorimeter in a chamber communicating with the atmosphere, and cooling the gas and the calorimeter to 20°); and in another case it is done at constant volume (by exploding the mixture in a bomb within a calorimeter and cooling the whole to 20°). *a.* Formulate the initial and final states in which the system exists in each of these two processes; using the symbols $T_1, T_2, p_1, p_2, v_1, v_2$, to represent initial and final conditions. *b.* Express the relation between the energy-content increase ΔE_p and the heat Q_p absorbed by the system in the first process, and the relation between the corresponding quantities ΔE_v and Q_v in the second process. *c.* Formulate a supplementary process (Process III) which when combined with the first (constant-pressure) process would result in the same change in state as occurs in the second (constant-volume) process; and express the relation between ΔE_{III} and Q_{III} for this process. *d.* By applying the first law of thermodynamics formulate an expression for the difference $Q_p - Q_v$ between the heat-quantities absorbed in the first and second processes.

Note. — Always formulate clearly and precisely the changes in state and attendant energy effects; for example, by tabulating them under headings as follows:

Process	Initial State				Final State				Energy-Effects		
	Composition	T	p	v	Composition	T	p	v	Q	W	E ₂ - E ₁

In formulating thermodynamic expressions for energy effects attending various changes in state, it is generally advantageous to replace the energy-content E by the energy function $E + pv$. The quantity $E + pv$, like the quantity E , is a property of the system which always has a definite value when the system is in a definite state; for it is evident that the pressure p and the volume v , as well as the energy-content E , have values which are determined by the state of the system. Hence this quantity changes in value by a definite amount when the system changes from one state to another, whatever be the process by which the change in state is brought about. In other words, a law of initial and final states applies to the change in the quantity $E + pv$, just as it does to the change in the quantity E . For brevity this quantity $E + pv$ is represented by a single letter H , and is called the *heat-content* of the system; but it should be understood that this name is a purely conventional one which does not imply that the energy quantity denoted by it is heat, any more than the name energy-content implies it. That is, by definition:

$$H = E + pv. \quad (17)$$

Expressions for the energy-content principles previously considered and for the corresponding principles, derivable from them, pertaining to heat-content, are formulated in Table I.

TABLE I. GENERAL EXPRESSIONS FOR INCREASE IN ENERGY-CONTENT AND IN HEAT-CONTENT.

<i>Applicable to</i>	<i>In Terms of Energy-Content</i>	<i>In Terms of Heat-Content</i>
Any infinitesimal change in state	dE	$dH = dE + d(pv)$
Any infinitesimal process	$dE = dQ - dW$	$dH = dQ - dW + d(pv)$
Any infinitesimal process producing no work except expansion work	$dE = dQ - p dv$	$dH = dQ + v dp$
A finite process at constant volume producing no work	$E_2 - E_1 = Q_v$	$H_2 - H_1 = Q_v + v(p_2 - p_1)$
A finite process at constant pressure producing no work except expansion work	$E_2 - E_1 = Q_p - p(v_2 - v_1)$	$H_2 - H_1 = Q_p$

These expressions need not be memorized, since any of them can be at once written down when the fundamental concepts are understood, as shown in Prob. 9.

Prob. 9. — Derivation of the Expressions for Heat-Content Increases. — Derive all the heat-content expressions given in Table I from the definition of heat-content $H = E + p v$, the fundamental first-law equation $dE = dQ - dW$, and the expression $dW = p dv$ for the maximum work attending volume changes (here called the *expansion work*.)

These expressions are more fully illustrated in the three following articles by applying them to typical changes in the state of systems; but some important characteristics of them will be here mentioned.

Table I shows that the heat Q_v absorbed by the system in a process taking place at constant volume directly measures the increase in the energy-content of the system undergoing such a process, and that the heat Q_p absorbed by the system in a process taking place at constant pressure directly measures the increase in the heat-content of the system undergoing such a process. That is:

$$E_g - E_l = Q_v. \quad (15)$$

$$H_g - H_l = Q_p. \quad (18)$$

This simple relation does not imply, however, that the use of heat-content is confined to processes at constant pressure—any more than that the use of energy-content is confined to processes at constant volume. In fact, for *any* change in state brought about by any process that produces no work other than that attending volume changes, just as the increase in energy-content is found by applying to the process the equation $dE = dQ - p dv$ (Eq. 13), so the increase in heat-content may be evaluated by applying to it the analogous equation:

$$dH = dQ + v dp. \quad (19)$$

Before concluding these general energy considerations, it is desirable also to state and formulate the fairly obvious principle, that the energy-content or heat-content of any pure homogeneous substance is fully determined by specifying its pressure and temperature. This is true since the state in general

of such a system is so determined (I, 13). This principle is expressed in the form of partial derivatives (I, 13) as follows:

$$dE = \left(\frac{\partial E}{\partial p} \right)_T dp + \left(\frac{\partial E}{\partial T} \right)_p dT. \quad (20)$$

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT. \quad (21)$$

7. Changes in Heat-Content Attending Changes in the Aggregation-State of Pure Substances at Constant Pressure and Temperature. — Especially important in physicochemical considerations are the changes in the state of aggregation of pure substances at a constant pressure and temperature (I, 18). Processes by which such changes are brought about are the isothermal vaporization of a liquid or sublimation of a solid substance at a constant pressure equal to its vapor-pressure; the isothermal fusion of a solid at its melting-point under a specified pressure, and the transition of one crystalline state of a substance into another at its transition-temperature and pressure, such as the conversion of rhombic sulfur into monoclinic sulfur at 95.6° and one atmosphere. The heat Q_p absorbed by such a process, called the *heat of vaporization, sublimation, fusion, or transition*, is evidently equal to the increase in heat-content $H_2 - H_1$ in the substance itself, since the process is one taking place at constant pressure. This heat-content increase will always be represented by ΔH , with the addition of a small capital letter as subscript when it is necessary to indicate whether the process is one of vaporization, sublimation, fusion, or transition; thus ΔH_v , ΔH_s , ΔH_f , ΔH_{tr} .

Throughout this book, as is done here, the symbol Δ preceding the symbol of any property determined by the state of a system (for example, ΔE , ΔH , Δv , $\Delta(pv)$, ΔN) will be used to denote the increment (whether positive or negative in value) which that property undergoes in any isothermal process or change in state under consideration: it is the difference obtained by subtracting from the value (E_2 , H_2 , v_2 , p_2v_2 , N_2) of the property in the final state of the system its value (E_1 , H_1 , v_1 , p_1v_1 , N_1) in its initial state. The limitation of the use of this general mathematical symbol for increment to that occurring in isothermal processes is a special convention adopted here for the sake of greater clearness.

Prob. 10. — Heat of Fusion and Heat-Capacity Illustrated. — Into 100 g. of water supercooled to -5° under the pressure of the atmosphere a minute fragment of ice is introduced, causing enough of the water to freeze to bring the mixture to the freezing-point. This process is adiabatic, since it is so rapid that there is no interchange of heat with the containing vessel. The heat of fusion of ice is 79.7 cal. per gram, and the specific heat-capacity of water between 0° and -5° is 1.013 cal. per degree. *a.* Specify the change in state resulting from this process and the attendant increase in the heat-content of the system. *b.* Describe a second process of bringing about the same change in state consisting of two steps suggested by the above heat data. *c.* With the aid of the heat-content relations calculate the quantity of ice which separates in the first (adiabatic) process. *Ans.* 6.36 g.

8. Changes in Energy-Content and in Heat-Content Attending Changes in the Temperature of Systems. — Expressions for the heat-effects attending changes in the temperature of a system in terms of its heat-capacities have already been given (Eqs. 9, 10; II, 4). Similar expressions can readily be formulated for the corresponding changes in the energy-content and in the heat-content of a system. This is important because these properties, rather than the heat effects attending particular processes, are employed in chemical thermodynamics for the reason that they are characteristic of the state of the system, thus of its temperature, aggregation-state, and chemical condition.

It is obvious that the increase in the energy-content of a system heated at constant volume is simply equal to the heat thereby absorbed (since no work is done), and therefore that its increase in energy-content per degree is equal to its heat-capacity at constant volume; that is,

$$(\partial E / \partial T)_v = C_v. \quad (22)$$

Moreover, it evidently follows from the definition of heat-content, which shows that $H_2 - H_1 = E_2 - E_1 + p_2 v_2 - p_1 v_1$, and from the first-law equation, which for heating at constant pressure takes the form $Q = E_2 - E_1 + p(v_2 - v_1)$, that the increase in heat-content of a system heated at constant pressure is simply equal to the heat thereby absorbed, and therefore that its increase in heat-content per degree is equal to its heat-capacity at constant pressure; that is,

$$(\partial H / \partial T)_p = C_p. \quad (23)$$

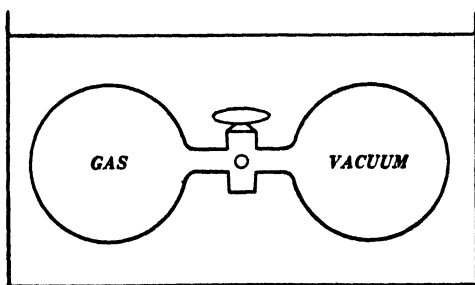
Prob. 11. — Change of Heat-Content and Energy-Content with Temperature and State of Aggregation. — a. From heat data previously given relating to water and from the value of the mean calorie (*I, 11*), calculate the difference in calories in the heat-content of 1 H₂O when in the state of vapor at 100° and 1 atm. and when in the state of ice at 0° and 1 atm. *b.* Calculate the difference in its energy-content when in these two states.

**** Prob. 12. — Change in the Energy-Content of a System Heated at Constant Pressure and in the Heat-Content of a System Heated at Constant Volume. —** Derive partial-derivative expressions for the two changes named in the problem title, namely for $(\partial E/\partial T)_p$ and for $(\partial H/\partial T)_v$, in terms of the appropriate heat capacity and such other quantity as is involved.

9. Energy-Content and Heat-Content of Perfect Gases. —

Besides the laws expressing the pressure-volume-temperature relations of perfect gases (*I, 14*), there is another law of perfect gases, one relating to their energy-content, which has been of great importance in the development of the science of thermodynamics. Namely, experiments have shown that, when a perfect gas in surroundings at the same temperature expands without producing work, no heat is given to or taken from the surroundings (*Gay-Lussac, 1807; Joule, 1845*). For example, when a perfect gas expands within a water calorimeter from one vessel into another vessel previously evacuated, as illustrated in Fig. 2, there is no change in the temperature of the calorimeter.

FIGURE 2. HEAT OF EXPANSION OF GASES.



These experiments lead to the following conclusion, here called the *energy-content law of perfect gases*: The energy-content of a definite quantity of a perfect gas remains unchanged when the gas changes its volume and pressure at a constant temperature.

That is, for the isothermal expansion of a perfect gas:

$$E_s - E_t = \Delta E = 0. \quad (24)$$

Since the heat-content of any system differs from its energy-content by its pressure-volume product, and since in the expansion of a perfect gas there is no change in the value of this product, a corresponding law applies to the change in heat-content. That is, for isothermal expansion of a perfect gas:

$$H_s - H_t = \Delta H = 0. \quad (25)$$

These laws lead to the corollary, important in thermodynamic derivations, that in any process in which a perfect gas expands at a constant temperature against any applied pressure (between zero and the pressure of the gas), a quantity of heat is withdrawn from the surroundings equal to the work produced. That is, since $E_s - E_t = 0$, for isothermal expansion of a perfect gas:

$$Q = W. \quad (26)$$

The energy-content law may also be stated as follows: The energy-content or heat-content of any specified quantity of any definite perfect gas is independent of its pressure and volume, and is determined only by its temperature. In this respect a perfect gas differs from homogeneous substances in other physical states; for, to determine their energy-content or heat-content, it is necessary to specify the pressure in addition to the temperature (Eqs. 20, 21; II, 6).

This statement leads to the following corollary. The increase per degree in the energy-content or in the heat-content of any definite system in the state of perfect gas has the same value whatever be its initial volume or pressure, and whether it be heated at constant volume or at constant pressure or otherwise; and therefore the molar heat-capacity of any definite perfect gas at constant volume or at constant pressure is independent of its volume and pressure, and is determined only by the temperature. That is, in functional notation (I, 13), for any definite system in the perfect-gas state (whatever its pressure or volume):

$$dE/dT = f(T); \quad \text{and} \quad dH/dT = f(T). \quad (27)$$

$$\tilde{C}_v = f(T); \quad \text{and} \quad \tilde{C}_p = f(T). \quad (28)$$

It can also readily be shown that the molar heat-capacity of any perfect gas at constant pressure is greater than that at constant volume by an amount equal to the gas-constant R , whatever be the gas or whatever be its temperature or pressure. That is,

$$\tilde{C}_p - \tilde{C}_v = R, \text{ for a perfect gas.} \quad (29)$$

Prob. 13. — Relation between the Two Heat-Capacities of a Perfect Gas. — Derive the equation $\tilde{C}_p - \tilde{C}_v = R$ by considering the energy-content increases that occur when one mol of a perfect gas changes by two different processes from an initial state characterized by p , v , and T to a final state characterized by p , $v + dv$, and $T + dT$.

Prob. 14. — Relation between Heats of Reaction at Constant Pressure and at Constant Volume. — Derive an expression and a numerical value in calories for the difference between the reaction heats Q_p and Q_v absorbed in the formation of 1 mol CO_2 from carbon monoxide and oxygen by the two processes described in Prob. 8 (II, 6), considering all three substances to be in the state of a perfect gas.

The extent to which actual gases at pressures up to one or two atmospheres deviate from the energy-content law of perfect gases will be considered later (*Ch. III*) in connection with a more exact experimental method of determining the change in energy-content. As an indication of the magnitudes involved, it may, however, be here mentioned that in expanding at 20° from two atmospheres to one atmosphere one mol of carbon dioxide increases its energy-content by 6.6 calories. This quantity may be compared with the maximum work producible by this expansion, which is approximately 404 calories (Prob. 3; II, 3), and with the energy-content increase $\tilde{C}_v$ attending a rise of 1° in the temperature of the gas, which at 20° is 6.8 calories.

The considerations of this article show that there are two experimentally distinct criteria which are fulfilled by a substance that is considered to be in the *perfect-gas-state*, defined as state as $p \doteq 0$. Namely, its pressure-volume-temperature relations are expressed by the equation $pv = NRT$; and its energy-content E (or its heat-capacity C_v) is independent of its pressure or volume and a function solely of the temperature. It is not, however, a necessary criterion of the perfect-gas state, as above defined, that its heat-capacity C_v have the same value at different temperatures.

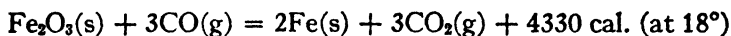
II. THE FIRST LAW OF THERMODYNAMICS APPLIED TO THERMOCHEMISTRY.

10. Expression of Changes in Heat-Content by Thermochemical Equations.—The branch of chemistry dealing with the heat-effects attending chemical changes is called *thermochemistry*. There is difference of usage regarding the sign of such heat-effects. When heat is actually evolved by the reaction, the heat of reaction is usually given a positive sign in thermochemical considerations, but a negative one in thermodynamic considerations. In this book a uniform convention, corresponding to the thermodynamic one, is employed; values of the heat-effects Q being always taken positive when heat is absorbed by the system from the surroundings, as in the vaporization of water, and taken negative when heat is given off (or evolved) by the system to the surroundings, as in the combustion of hydrogen and oxygen.

It has already been pointed out (II, 5) that the heat of a reaction is usually interpreted as the heat-effect in the surroundings (heat evolution or absorption) when the reaction takes place at constant pressure and temperature with production of no work except expansion work. Furthermore, it was shown (II, 6) that the heat withdrawn from the surroundings Q_p during such a process measures directly the increase in heat-content ΔH of the reacting mixture. Correspondingly, the heat withdrawn Q_v when the reaction takes place at constant volume and temperature with production of no work measures directly the increase in energy-content ΔE of the reacting mixture. Finally, it was shown (Prob. 14; II, 9) that the difference $Q_p - Q_v$ between these two effects is substantially equal to the expansion work attending the constant pressure process.

In order to express changes in heat-content that attend chemical reactions at any constant temperature and pressure, heat-content equations are conveniently employed. In the equation written in the usual way to show the change in state, the chemical formulas of the substances are considered to denote their heat-contents; and, to make the heat-content equation balance, there is inserted on the right-hand side a numerical term equal to the heat-content decrease $-\Delta H$ which attends the reaction.

For example, the expression



signifies that at 18° the sum of the heat-contents of the specified reaction-products is less than the sum of the heat-contents of the specified reacting substances by 4330 cal.; in other words, that ΔH for the specified reaction at 18° is -4330 cal. The pressure is understood to be one atmosphere unless otherwise stated.

The state of aggregation of each substance is shown as usual (*I, 12*) by affixing to its formula the letter *s*, *l*, or *g* within parentheses. When solids are capable of existing in different allotropic or crystalline forms, the special form involved is specified; for example *C* (graphite), *S* (rhombic).

When a substance is dissolved in water, the heat-content of the solution is expressed by attaching $x\text{Aq}$ to the formula of the solute; thus the heat-content of a solution of 1 *KCl* in 100 H_2O is represented by $\text{KCl} \cdot 100\text{Aq}$; and the heat-effect attending the process of solution at 18° is expressed by the heat-content equation:



When the substance is dissolved in so large a quantity of water that the addition of more water produces no appreciable heat-effect, the symbol ∞Aq may be attached to the formula of the substance.

These heat-content equations can be treated strictly as algebraic equations, and can be combined with one another by addition or subtraction; for every quantity in them has a definite value (namely, that of the heat-content of the substance represented by the formula), irrespective of the other quantities that occur with it in the equation.

Because of radiation errors the heat-effects can be directly determined by calorimetric measurements only for those chemical changes which take place completely within a few minutes. But the heat-effects of many other reactions can be calculated from those which have been directly measured, by applying the law that the total change in heat-content is dependent only on the initial and final states of the system. This method is extensively employed in thermochemistry. It is exemplified by Probs. 16, 17, and many subsequent problems.

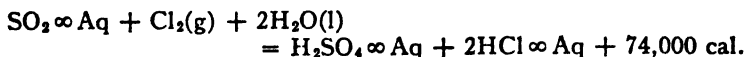
*Expression of Heat Data and Calculation of
Heats of Reactions by Heat-Content
Equations.*

Prob. 15. — The union at 18° and 1 atm. of 1 g. of aluminum with oxygen is attended by a heat evolution of 7040 cal.; and the union of 1 g. of β graphite with oxygen to form carbon monoxide is attended by a heat evolution of 2250 cal. Express these data in the form of heat-content equations; and calculate from them the heat of the reaction $\text{Al}_2\text{O}_3(\text{s}) + 3 \text{C}(\beta \text{ graphite}) = 2 \text{Al}(\text{s}) + 3 \text{CO}(\text{g})$ at 18°.

Prob. 16. — *a.* Express the following data at 18° in the form of heat-content equations, employing the conventions described in the preceding text. The formation of 1 mol of gaseous HCl from the elementary substances evolves 22,060 cal. Its solution in 100 formula-weights of water evolves 17,320 cal. By the reaction between 1 mol of gaseous chlorine and a solution of 2 formula-weights of HI in 200 formula-weights of water, forming solid iodine and a dilute HCl solution, 52,240 cal. are liberated. The solution of 1 mol of gaseous HI in 100 formula-weights of water evolves 19,170 cal. *b.* By combining these equations, calculate the heat absorbed when 1 mol of gaseous HI is formed out of gaseous hydrogen and solid iodine at 18°.

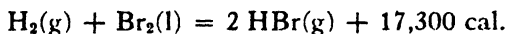
Prob. 17. — *a.* Express the following data (referring to 18°) in the form of heat-content equations: The solution of 1 $\text{SO}_2(\text{g})$ in a large quantity of water evolves 8000 cal.; 1 mol of $\text{Cl}_2(\text{g})$ acting on this solution (with production of a dilute solution of HCl and H_2SO_4) evolves 74,000 cal.; the union of 1 $\text{H}_2(\text{g})$ with $\frac{1}{2} \text{O}_2(\text{g})$ to form liquid water evolves 68,370 cal.; the union of $\frac{1}{2} \text{H}_2(\text{g})$ with $\frac{1}{2} \text{Cl}_2(\text{g})$ evolves 22,060 cal.; the heat of solution of 1 $\text{HCl}(\text{g})$ in a large quantity of water is - 17,400 cal.; and that of 1 $\text{H}_2\text{SO}_4(\text{l})$ is - 18,000 cal. *b.* With the aid of these data, find the value in calories of ΔH for the change in state, $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) = \text{H}_2\text{SO}_4(\text{l})$.

Note: Even when $\infty \text{ Aq}$ occurs, there must be included in the heat-content equation the number of H_2O 's required to make the chemical balance; thus the second of the above heat-effects should be expressed by:



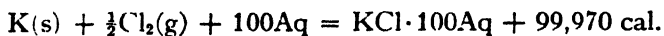
11. Heats of Formation in Relation to Heats of Reaction. — Although only changes in heat-content can be determined, yet it is convenient to employ an arbitrary scale of heat-contents which has as its zero-points the heat-contents of the

various elementary substances at the temperature under consideration, at a pressure of 1 atmosphere, and in the state of aggregation which is stable at this temperature and pressure. Under this convention the molar (or formular) heat-content ($\bar{H}$) of any compound substance is evidently equal to the increase in heat-content (ΔH), commonly called its heat of formation,* which attends its formation out of the elementary substances. For example, the heat-content at 18° of one mol of gaseous hydrogen bromide, or the numerical value of the formula 1 HBr(g) in a heat-content equation is - 8650 cal.; for this is the heat absorbed when it is formed out of gaseous hydrogen and liquid bromine at 18°. This also follows at once from the heat-content equation



for when one puts, in accord with the convention, $\text{H}_2(\text{g}) = 0$ and $\text{Br}_2(\text{l}) = 0$, there results $\text{HBr}(\text{g}) = - 8650 \text{ cal.}$

Similarly the heat-content of a potassium chloride solution represented by the formula $\text{KCl} \cdot 100 \text{ Aq}$ at 18° is - 99,970 cal.; for this is the sum of the heat (- 104,360 cal.) absorbed when one formula-weight of solid KCl is formed out of solid potassium and gaseous chlorine at 18° and of the heat (4390 cal.) absorbed when the salt is dissolved in 100 formula-weights of water at 18°. This value is also directly obtained from the following equation which expresses these thermochemical data:



For putting $\text{K}(\text{s}) = 0$, $\text{Cl}_2(\text{g}) = 0$, and $\text{Aq} = 0$, there results $\text{KCl} \cdot 100 \text{ Aq} = - 99,970 \text{ cal.}$

It is to be noted that in heat-content equations the symbol $x \text{ Aq}$ (not attached to another formula) has, like the formulas of elementary substances, the value zero; for the water represented by it is considered not to have been formed out of its elements. Water which has been so formed (see note to Prob. 17) is represented by the formula $x \text{ H}_2\text{O}$.

It is evident that the employment of heats of formation greatly simplifies the task of determining and systemizing ther-

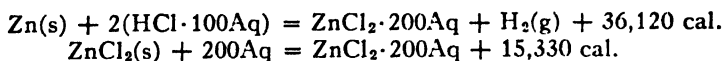
* In this book, as stated in the preceding article, such terms as *heat of formation*, *solution*, *vaporization*, *fusion*, *neutralization*, *ionization*, etc., always signify the *heat absorption* or the *increase in heat content* that attends the change in the system denoted by the name when this change takes place under a *constant pressure* of one atmosphere (unless otherwise specified).

mochemical data; for instead of measuring and recording the change in heat-content attending every chemical reaction, it suffices to do this for the formation of every compound out of the corresponding elementary substances. The exact experimental determination of the heats of formation of as many compound substances as possible thereby becomes of great importance. An example of the indirect methods often resorted to has been given in Prob. 16 above; and the following problems afford further illustrations.

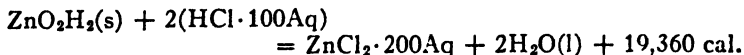
*Heats of Formation (Heat-Content Values)
Derived from Measured Heats of Reactions.*

Prob. 18. — The combustions at 18° and 1 atm. of 1C (diamond), of 1H₂(g), and of 1C₂H₂ (acetylene gas) with formation of carbon dioxide and liquid water at 1 atm. evolve 94,450 cal., 68,370 cal., and 311,100 cal., respectively. Formulate these three heat-effects in heat-content equations, and tabulate the heat-contents at 18° of 1CO₂(g), 1H₂O(l), and 1C₂H₂(g).

Prob. 19. — Find the heat-content of ZnCl₂(s) and of ZnCl₂·200Aq at 18° from the needed data given in Prob. 16, and the following heat-content equations at 18°:



Prob. 20. — Calculate the heat of formation of 1ZnO₂H₂(s) at 18° from the following equation and the other needed data given in preceding problems:



Prob. 21. — Calculate the heat of formation of 1H₂SO₄(l) at 18° from the data given in Prob. 17 and the heat of formation of 1SO₂(g), which is 70,920 cal. evolved.

The numerical values of the heats of formation (or heat-contents) of all the compounds for which data are available are recorded in tables of physical and chemical constants such as the International Critical Tables.* These values may be substituted

* The heats of reaction given in the text and problems were in most cases computed from the heats of formation at 18° compiled by F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (1936). These authors have selected diamond as the (only truly reproducible) form of carbon to which the heat-contents of the other forms of carbon (α graphite, β graphite, amorphous "charcoal," etc.) and of carbon compounds are referred.

for the corresponding chemical formulas in any heat-content equation, and the heat of any reaction involving them may thus be calculated. This is equivalent to considering that the reaction takes place by the indirect process of first decomposing the reacting compounds into their elementary substances and then combining them to form the reaction-products. For example, to find the heat of the gas reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, the reaction may be considered to take place in the three stages $\text{CO(g)} = \text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)}$, $\text{H}_2\text{O(g)} = \text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$, $\text{C(s)} + \text{O}_2\text{(g)} = \text{CO}_2\text{(g)}$, and the sum taken of three heat-content increases that attend these separate stages.

Heats of Reactions Calculated from Heat-Content Values.

Prob. 22. — Calculate at 18° the heat of the reaction $4\text{HCl(g)} + \text{O}_2\text{(g)} = 2\text{Cl}_2\text{(g)} + 2\text{H}_2\text{O(g)}$ (involved at higher temperatures in the Deacon process of making chlorine) from the heats of formation of 1HCl(g) and $1\text{H}_2\text{O(g)}$ at 18° which are $-22,060$ cal. and $-57,800$ cal., respectively.

Prob. 23. — Calculate at 18° the heat-content increase ΔH of the reaction $4(\text{HCl} \cdot 100 \text{ Aq}) + \text{O}_2\text{(g)} = 2\text{Cl}_2\text{(g)} + 2\text{H}_2\text{O(l)} + 400 \text{ Aq}$ from the result of Prob. 22 and other data needed, which are obtainable from previous problems.

Prob. 24. — *Heat of a Reaction Involving Organic Compounds Calculated from Their Heats of Combustion.* — Calculate the heat of the reaction $\text{C}_2\text{H}_5\text{OH} \infty \text{ Aq} + \text{O}_2\text{(g)} = \text{CH}_3\text{COOH} \infty \text{ Aq} + \text{H}_2\text{O(l)}$ at 18° from the facts that the combustion of $1\text{C}_2\text{H}_5\text{OH(l)}$ and of $1\text{CH}_3\text{COOH(l)}$ evolves $326,870$ cal. and $208,300$ cal., respectively, and that their solution in a large quantity of water evolves 2680 cal. and 350 cal., respectively.

Note. — This problem illustrates the fact that the heat-effects that attend the conversion of organic compounds into one another, being seldom directly measurable, are commonly derived from their heats of combustion. From these heats of combustion the heats of formation of the compounds out of their elementary substances may be calculated; but when such heats of formation have not already been computed, the heat-content equations expressing the heats of combustion may be formulated and then so combined as to give the desired heat of reaction.

12. The Heat of Solution and of Dilution of Substances.

— It is evident from preceding illustrations that the heat of solution of substances is an important quantity in thermochemi-

cal calculations. In determining and expressing it the quantity of solvent in which a definite weight of the substance is dissolved must be taken into consideration. The two limiting cases are the heats of solution in a very large quantity of solvent and in that quantity of solvent which forms with the substance a saturated solution. These two heat-effects sometimes have different signs. They evidently differ by the heat of dilution of the saturated solution with a large quantity of water.

The dissolving of gaseous substances in water is always attended by an evolution of heat; and the dissolving of solid substances in solvents is usually attended by an absorption of heat. The mixing of liquids may be attended either by evolution or absorption of heat, as explained later (IV, 37).

The heat of dilution of substances in solution is also important; for it enables the heat of formation of a solution of one concentration to be calculated from that of a solution of another concentration, and thus enables heats of reaction to be calculated at different concentrations. The heat-effect attending the addition of an equal volume of water to a concentrated aqueous solution is often large, but it becomes less as the concentration diminishes; and, after a moderately small concentration (such as 0.2 formal) has been attained, there is usually only a very small heat-effect on adding even a very large quantity of water. For example, on adding at 18° to 1 formula-weight of gaseous HCl or of solid ZnCl_2 successively ΔN formula-weights of water, there are evolved the following quantities of heat ($-Q_p$) in calories:

ΔN	5	5	10	30	50	100	200
$-Q_p$ for HCl.....	15040	1250	570	337	125	83	60
$-Q_p$ for ZnCl_2	7650	1860	1310	2180	1500	830	390

Prob. 25. — Heat of Transition Derived from Heats of Solution. — The heat of solution at 18° in a large quantity of chloroform of 1 at.wt. of rhombic sulfur is 640 cal., and of 1 at.wt. of monoclinic sulfur is 560 cal. Show, by applying the law of initial and final states, what other heat-effect can be derived from these data, and what its value is.

Prob. 26. — Heat of Fusion Derived from Heats of Solution. — At 7° the heat of solution of $1\text{CH}_3\text{COOH}(s)$ in a large quantity of water is 2130 cal., and that of $1\text{CH}_3\text{COOH}(l)$ is -400 cal. Calculate the heat of fusion at 7° of 1 gram of acetic acid.

Prob. 27. — Change of Heat of Reaction with the Concentration. — The heat of solution at 18° of 1Zn(s) in the required amount of dilute hydrochloric acid of the composition 1HCl·200Aq is — 34,810 cal. Find its heat of solution in more concentrated hydrochloric acid of the composition 1HCl·5Aq, *a.* by applying the law of initial and final states, and *b.* by formulating the heat-content equations involved.

13. Heats of Reaction in Aqueous Solution. — The investigations made of the heat-effects attending chemical reactions in aqueous solution between substances present at fairly small concentrations (0.1–0.3 normal) have established the following principles:

(1) On mixing solutions of two neutral salts which do not form a precipitate by metathesis (for example, solutions of potassium chloride and sodium sulfate) there is scarcely any heat-effect. Exceptions to this principle are met with in the few cases in which an unionized salt is produced by the metathesis. Thus the metathetical reaction $2\text{K}^+\text{Cl}^- + \text{Hg}^{++}(\text{NO}_3^-)_2 = 2\text{K}^+\text{NO}_3^- + \text{HgCl}_2$ is attended by a heat-evolution of 12,400 cal.

(2) The heat of neutralization of a solution of any strong monobasic acid with a solution of any strong monacidic base (for example, of hydrochloric acid, nitric acid, etc., with sodium hydroxide, potassium hydroxide, etc.) has approximately the same value, whatever be the acid or base. At 18° this nearly constant value averages — 13,800 cal. per equivalent when the acid and base solutions are 0.12 to 0.25 normal.

(3) When the base or acid is weak (as in the case of ammonium hydroxide or hydrofluoric acid), the heat-effect attending its neutralization with strong acid or base is often much larger or smaller than that observed when both acid and base are strong; thus the heat of neutralization of one equivalent of ammonium hydroxide with one of hydrochloric acid is — 12,300 cal., and that of one equivalent of hydrofluoric acid with one of sodium hydroxide is — 16,300 cal.

(4) When one formula-weight of a dibasic acid is neutralized in steps by adding first one equivalent of a strong base and then a second equivalent, the heat-effects for the two equivalents of base are usually different; for example, at 18° the two heats of reaction are — 14,600 and — 16,600 cal. in neutralizing 0.28

normal sulfuric acid solution with 0.28 normal sodium hydroxide solution, and they are $-11,100$ and -9100 cal. in neutralizing carbonic acid with that base.

(5) When certain polybasic acids are neutralized, there is sometimes scarcely any heat-effect when the second or third equivalent of base is added. Thus the successive heats of neutralization when phosphorous acid (H_3PO_3) is treated with sodium hydroxide at 18° are: $-14,800$ cal. with the first equivalent, $-13,600$ cal. with the second equivalent, and only -500 cal. with the third equivalent; and with hypophosphorous acid (H_3PO_2) the heat of neutralization is $-15,200$ cal. with the first equivalent of sodium hydroxide, and only -110 cal. with the second equivalent.

(6) With certain polybasic acids there is a considerable heat-effect when to the solution of the neutral salt another equivalent of base is added; thus, there is a heat-evolution of 1200 cal. on mixing a solution containing one equivalent of sodium hydroxide with one containing one formula-weight of sodium phosphate (Na_3PO_4).

Interpretation of the Heats of Reaction in Aqueous Solution.

Prob. 28. — *a.* Explain principle (1) stated in the preceding text with the aid of the ionic theory (I', 1), which assumes that salts, strong acids, and bases in dilute aqueous solution are completely dissociated, and that weak acids and bases are only partly dissociated into electrically charged molecules or ions. *b.* Write a heat-content equation corresponding to the ionic reaction to which the heat-effect is mainly due in the reaction cited as an exception to the principle.

Prob. 29. — Show that on mixing dilute solutions of two salts (such as lead nitrate and potassium iodide) which form a precipitate by metathesis there must be a heat-effect which is substantially equal, but opposite in sign, to the heat of solution of the precipitated substance (the lead iodide).

Prob. 30. — *a.* Write the ionic reaction to which the nearly constant heat of neutralization of strong acids and bases corresponds. *b.* State what other heat-effect is involved in the neutralization of ammonium hydroxide with a strong acid, and find its value. *c.* What is the heat-effect that attends the reaction between $1 \text{ NH}_4\text{Cl}$ and 1 NaOH in 0.2 normal solution?

Prob. 31. — Calculate the heat of ionization of 1 HF from the facts that its heat of neutralization in 0.28 normal solution with 0.28 normal NaOH solution has been found to be $-16,300$ cal., and its ionization in 0.28 normal solution is estimated to be 5.2%.

Prob. 32. — Calculate the heats of ionization at 18° , *a.* of H_2CO_3 , and *b.* of HCO_3^- from the heats of neutralization of carbonic acid given in paragraph (4). Carbonic acid is a very slightly ionized acid; sodium hydrogen carbonate solution is practically neutral; and the sodium carbonate in the 0.07 formal solution produced by the neutralization is 6.3% hydrolyzed with formation of NaOH and NaHCO_3 .

Prob. 33. — State what the observed heat-effects, given in paragraph (5), attending the neutralization of phosphorous acid and of hypophosphorous acid show as to the existence of salts of these acids in solution.

Prob. 34. — Explain the fact, stated in paragraph (6), that there is a large heat-effect on adding a solution of NaOH to one of Na_3PO_4 .

Prob. 35. — *Determination of Chemical Equilibria by Thermochemical Methods.* — Describe a thermochemical method of determining the extent to which acetic acid displaces hydrofluoric acid from sodium fluoride in dilute solution. The heat of neutralization of acetic acid with sodium hydroxide at 18° is $-13,230$ cal., and that of hydrofluoric acid is $-16,300$ cal.

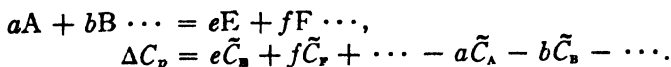
14. Effect of Temperature on the Heat of Reactions. — Owing to radiation errors, heats of reaction can be directly measured in a calorimeter only at temperatures not far removed from the room temperature. It is, however, possible to calculate the heats of reactions at other temperatures with the aid of heat-capacity data and other heat data, as will now be described.

Consider for definiteness a specific reaction, such as $\text{C(s)} + \text{CO}_2(\text{g}) = 2\text{CO(g)}$, occurring at a constant pressure p in one case at the temperature T , and in another case at the temperature $T + dT$. Let the heat-contents of the system in its initial state (in the state of carbon and CO_2 gas) be H_i at T , and $H_i + dH_i$ at $T + dT$; and the heat-contents in its final state (in the state of CO gas) be H_f at T , and $H_f + dH_f$ at $T + dT$. The increases in heat-content attending the reaction will then be: $H_f - H_i = \Delta H = Q_p$ at T ; and $(H_f + dH_f) - (H_i + dH_i) = \Delta H + d\Delta H = Q_p + dQ_p$ at $T + dT$. Hence, $(\partial\Delta H/\partial T)_p = (\partial H_f/\partial T)_p - (\partial H_i/\partial T)_p = dQ_p/dT$. The two partial deriva-

tives in the second member are, however, the heat-capacities C_{p_2} and C_{p_1} at constant pressure of the system in its final and its initial states, respectively (II, 8). Introducing these quantities, transforming, and writing ΔC_p for $C_{p_2} - C_{p_1}$ (in accord with the practice of representing by $\Delta(x)$ the increase in the value of any property x that attends an isothermal change in state), there results, for constant pressure conditions:

$$d\Delta H = \Delta C_p dT; \quad \text{or} \quad dQ_p = \Delta C_p dT. \quad (30)$$

In order to apply this equation to specific reactions, ΔC_p must be evaluated. This may be done without error in case each phase involved consists of a pure substance or of a mixture of perfect gases, by regarding the heat-capacities of the system in its initial state or in its final state as the sum of the separate heat-capacities of the pure substances. Hence, for any chemical reaction



Here $\tilde{C}_e, \tilde{C}_f \cdots \tilde{C}_a, \tilde{C}_b \cdots$ are the molar (or formular) heat-capacities of the respective substances at constant pressure. In the case of mixtures of actual gases at a pressure not exceeding one atmosphere, the error involved in this assumption is usually inconsiderable.

In order to integrate Eq. 30, for example, for the purpose of deriving from values of ΔH and Q_p at room temperature, the corresponding values at a higher temperature, the separate values of $\tilde{C}_e, \tilde{C}_f \cdots \tilde{C}_a, \tilde{C}_b \cdots$ may be expressed as temperature-functions, best in the form $\tilde{C} = \tilde{C}_0 + \alpha T + \beta T^2 \cdots$ (II, 4); then by combination of the functions a corresponding one for ΔC may be obtained, which may be introduced in Eq. 30.

The heat-capacity of gases in relation to the complexity of their molecules will be considered in the next chapter. Here are recorded for future reference the empirical functions expressing the heat-capacities at constant pressure of various gases which were adopted by Lewis and Randall for general use in applied thermodynamics. These functions were based on measurements covering a temperature-range from 0° to 1000° or 2000° , and are

applicable for gases at moderate pressures. For further statements regarding them the reader is referred to the original text of Lewis and Randall.*

TABLE II. MOLAR-HEAT CAPACITIES AT CONSTANT PRESSURE.

Gas	Heat-Capacity Function
Any Monatomic	$\bar{C}_p = 5.0 + 0.0 T$
H ₂	$\bar{C}_p = 6.50 + 0.0009 T$
O ₂ , N ₂ , NO, CO, HCl, HBr, HI	$\bar{C}_p = 6.50 + 0.001 T$
Cl ₂ , Br ₂ , I ₂	$\bar{C}_p = 7.4 + 0.001 T$
H ₂ O, H ₂ S	$\bar{C}_p = 8.81 - 0.0019 T + 0.00000222 T^2$
CO ₂ , SO ₂	$\bar{C}_p = 7.0 + 0.0071 T - 0.00000186 T^2$
NH ₃	$\bar{C}_p = 8.04 + 0.0007 T + 0.0000051 T^2$
CH ₄	$\bar{C}_p = 7.5 + 0.005 T$

Effect of Temperature on the Heat of Reaction.

Prob. 36. — Calculate the heat of formation of 1 PbO(s) at 200° from the heat of formation at 18°, which is - 52,460 cal., and from the specific heat-capacities at constant pressure of lead, lead oxide, and oxygen, which have mean values of 0.032, 0.052, and 0.215 cal. per degree, respectively, between 18° and 200°. Assume (as a close approximation) that these mean heat-capacities are the true heat-capacities and are constant within this temperature interval.

Prob. 37. — The heat of the reaction $2\text{CO(g)} + \text{O}_2\text{(g)} = 2\text{CO}_2\text{(g)}$ at 18° is - 135,220 cal. *a.* Calculate the heat of this reaction at 1000° using the molar heat-capacity functions recorded in Table II. *b.* When ΔC is a function of the form $\Delta C_0 + \alpha T + \beta T^2$, show that the heat of the reaction ΔH at any temperature T is given by the general equation $\Delta H = \Delta H_0 + \Delta C_0 T + \frac{1}{2} \alpha T^2 + \frac{1}{3} \beta T^3$, where ΔH_0 is a constant of integration. *c.* Calculate the value of the constants ΔC_0 , α , β , and ΔH_0 , for the above reaction.

Note that the general expression for ΔH is limited to that range of temperature for which the heat-capacity function is valid.

Prob. 38. — *a.* Calculate the heat of the reaction $\text{C}(\beta \text{ graphite}) + \text{CO}_2\text{(g)} = 2\text{CO(g)}$ at 1000°C from the heats of formation of 1C(β graphite), 1CO₂(g), and 1CO(g) at 18° which are

* *Thermodynamics*, McGraw-Hill Book Co., New York (1923).

— 220 cal., — 94,450 cal., and — 26,840 cal., respectively, from the heat-capacity functions of Table II, and from the fact that the atomic heat-capacity of graphite is expressed by the function, $\tilde{C} = 1.1 + 0.0048 T - 0.000012 T^2$. *b.* From this result and that of Prob. 37*a*, calculate the heat of formation of 1CO(g) and of $\text{1CO}_2\text{(g)}$ (out of graphite and oxygen) at 1000° .

In deriving the change in the heat of reaction in the case that a phase of the system undergoes between the temperatures under consideration a change in the state of aggregation (thus in case a solid melts or undergoes transition or in case a liquid vaporizes), there must be taken into account not only the heat-effect attending this change in phase, but also the fact that the heat-capacity function for the substance involved is discontinuous.

In this case the clearest method of deriving the change in the heat of reaction is to conceive two different processes of converting the reacting substances at one temperature into the reaction-products at the other temperature and so apply the principle that the total heat-content change must be equal in the two processes.

For example, if a relation is desired between the heat of the reaction $\text{H}_2\text{(g)} + \text{I}_2\text{(s)} = 2\text{HI(g)}$ at 20° and 1 atm. and that of the reaction $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} = 2\text{HI(g)}$ at 200° and 1 atm., the two following processes of converting $\text{H}_2\text{(g)} + \text{I}_2\text{(s)}$ at 20° into 2HI(g) at 200° , carried out always at 1 atm., may be considered.

- I. *a.* Let $\text{H}_2\text{(g)} + \text{I}_2\text{(s)}$ react at 20° , forming 2HI(g) at 20° .
- b.* Heat 2HI(g) from 20° to 200° , yielding 2HI(g) at 200° .
- II. *a.* Heat $\text{H}_2\text{(g)}$ from 20° to 200° .
- b.* Heat $\text{I}_2\text{(s)}$ from 20° to 113.5° , the melting-point of $\text{I}_2\text{(s)}$.
- c.* Melt $\text{I}_2\text{(s)}$ at 113.5° .
- d.* Heat $\text{I}_2\text{(l)}$ from 113.5° to 184.3° , the boiling-point of $\text{I}_2\text{(l)}$.
- e.* Vaporize $\text{I}_2\text{(l)}$ at 184.3° .
- f.* Heat $\text{I}_2\text{(g)}$ from 184.3° to 200° .
- g.* Let $\text{H}_2\text{(g)} + \text{I}_2\text{(g)}$ react at 200° , forming 2HI(g) at 200° .

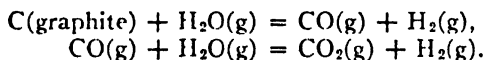
By evaluating and equating the heat-content increases attending these two processes a relation is obtained between the heats of the reaction at 20° and 200°. This relation evidently involves the heat of fusion of $I_2(s)$, the heat of vaporization of $I_2(l)$, and the heat-capacities of $H_2(g)$, $HI(g)$, $I_2(s)$, $I_2(l)$, and $I_2(g)$ between the temperatures through which these respective substances are heated.

*Effect of Temperature on the Heat of Reaction
when One or More of the Substances
Undergo a Change in Phase.*

Prob. 39. — Calculate the heat of the reaction $H_2(g) + I_2(g) = 2HI(g)$ at 200° and 1 atm. from the following data. The reaction $H_2(g) + I_2(s) = 2HI(g)$ absorbs 11,820 cal. at 18° and 1 atm. The fusion of $I_2(s)$ at its melting-point (113.5°) absorbs 4000 cal. The vaporization of $I_2(l)$ at its boiling-point (184.3°) and 1 atm. absorbs 10,200 cal. The mean formular heat-capacity is 13.3 cal. per degree for $I_2(s)$ between 18° and 113.5°, and 15 cal. per degree for $I_2(l)$ between 113.5° and 184.3°.

Prob. 40. — Calculate the heat of formation of $1H_2O(g)$ at 1000°C from the heat-capacity functions in Table II and the following data. The heat of formation of $1H_2O(l)$ at 18° is - 68,370 cal. Its vaporization at 100° absorbs 9720 cal.

Prob. 41. — From the heat-contents at 1000°C of $1CO(g)$, $1CO_2(g)$, and $1H_2O(g)$, as found in Probs. 38 and 40, calculate the heat evolved at 1000°C by the following chemical reactions:



15. Applications of Thermochemical Principles. — The problems in the following groups serve to illustrate some important applications of the first law of thermodynamics to industrial chemical operations. Thus the problems include the estimation of the maximum temperature produced by flames or by the explosion of gaseous mixtures, the determination of the quantity of heat produced in continuous chemical processes (whose removal to maintain constancy of temperature often constitutes one of the main difficulties of large-scale operation), and a consideration of the effectiveness of hot gases as an evaporating agent. Heat data which may be needed will be found in Table II and in previous problems of this section.

*Maximum Temperature Producible by Flames
and Explosions.*

Prob. 42. — Calculate the maximum temperature that could theoretically be attained in the flame produced by burning at 18° a "water-gas" consisting of equimolal quantities of hydrogen and carbon monoxide with twice the quantity of air required for complete combustion. Assume that the reaction-products are not appreciably dissociated, and that air contains 1 O_2 to 4 N_2 .

Prob. 43. — *a.* Calculate the maximum temperature and pressure that could be produced by the explosion within a bomb of a mixture consisting of 1 mol of H_2 , $\frac{1}{2}$ mol of O_2 , and 1 mol of N_2 at 18° and 100 mm., assuming that the water produced is not appreciably dissociated. *b.* The maximum pressure produced in an actual experiment was found to be 840 mm. Show how from this result the degree of dissociation of the water-vapor and the temperature of the mixture at the moment of the explosion can be calculated. (The equations should be formulated, but they need not be solved numerically.)

*Heat Evolved by Continuous Processes at
High Temperatures.*

Prob. 44. — In the Deacon process of making chlorine, a mixture of oxygen and hydrogen chloride in the proportion $\frac{1}{2} \text{O}_2 : 1 \text{HCl}$ at 18° is passed continuously into a vessel at 386° containing a suitable catalyzer. The gas is passed so slowly that equilibrium is established, 80% of the hydrogen chloride being converted into chlorine and water. Calculate the heat which will be given off from the equilibrium vessel per mol of HCl passed through, and which must, to maintain a constant temperature, be continuously withdrawn by a suitable system of cooling.

Prob. 45. — In the Grillot contact process of making fuming sulfuric acid a mixture of sulfur dioxide and air passes through a chamber containing a series of trays charged with the platinum catalyst. This mixture enters the chamber at 380° (the lowest temperature at which a rapid reaction will occur), and rises in temperature as a result of the heat of reaction. This rise in temperature must not exceed 100° , if considerable dissociation of the SO_3 is to be avoided. Calculate the smallest volume of air that may be present with one volume of sulfur dioxide in the gas entering the chamber at 380° in order that the rise of temperature may not exceed 100° . The heat of the reaction $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{SO}_3(\text{g})$ is $-22,000$ cal. at 380° . Consider the molar heat-capacity of each gas in the mixture to be the same as that of nitrogen or oxygen. Assume that 97% of the SO_2 is converted into SO_3 , and that there is no loss of heat by heat interchange.
Ans. 29 volumes.

Prob. 46. — Heat-Effects in the Process of Concentrating Sulfuric Acid by Hot Gases.—In the Gaillard process of concentrating sulfuric acid a 73% acid (corresponding to $1 \text{ H}_2\text{SO}_4 \cdot 2 \text{ H}_2\text{O}$) is sprayed at 18° into a brick-lined tower, and in falling through the tower is caused to meet an ascending current of hot producer-gas consisting (mainly) of nitrogen and carbon monoxide, which enters the bottom of the tower at 1100° and leaves the top at 200° . Calculate how many cubic meters of producer gas must be supplied per kilogram of the 73% acid to furnish the heat necessary to concentrate it to 91.5% H_2SO_4 (corresponding to $2 \text{ H}_2\text{SO}_4 \cdot 1 \text{ H}_2\text{O}$), assuming the latter leaves the tower at 200° , and that there is no loss of heat by radiation. The heat evolved ($-Q_p$) on adding $\text{NH}_2\text{O}(l)$ to $1 \text{ H}_2\text{SO}_4(l)$ at 18° has been calorimetrically determined, with the following results:

$\text{NH}_2\text{O}(l)$	0.5	1.0	2.0	5.0	10.0
$-Q_p$ (in cal.)	3750	6710	9760	13750	15880

The heat of vaporization of 1 g. of water at 100° is 540 cal. The mean specific heat-capacity of 91.5% H_2SO_4 between 18° and 200° is 0.4 cal. per degree. In solving this problem write the heat-content equations by which $1 \text{ H}_2\text{SO}_4 \cdot 2 \text{ H}_2\text{O}$ at 18° can be converted into $1 \text{ H}_2\text{SO}_4 \cdot \frac{1}{2} \text{ H}_2\text{O}$ and $1\frac{1}{2} \text{ H}_2\text{O}(g)$ at 200° .

III. THE SECOND LAW OF THERMODYNAMICS APPLIED TO CHANGES IN STATE AND PROCESSES AT A SINGLE TEMPERATURE.

16. Perpetual Motion of the Second Kind. — The first law of thermodynamics states that, when one form of energy is converted into another, the quantity of the form of energy that is produced is equivalent to the quantity of the form that disappears; but it does not indicate that there is any other restriction as to the transformability of the different forms of energy. However, experience has shown that, though the various forms of work can be completely transformed into one another and into heat, yet the transformation of heat into work is subject to certain limitations. One such limitation is expressed by the principle that heat is never transformed into work by any cycle of changes taking place in any system kept in surroundings at one definite temperature. By a *cycle of changes* is meant any series of changes in state of such a character that the system finally returns to its initial state. A process by which such a cycle of changes is brought about is called a *cyclical process*.

If a cycle of changes in state by which heat is transformed into work at constant temperature could be realized, the cycle could be indefinitely repeated and thereby produce from heat an unlimited quantity of work, thus constituting a form of perpetual motion, which may be called *perpetual motion of the second kind*. Such perpetual motion, by which work is conceived to be produced out of heat at constant temperature, is to be distinguished from perpetual motion of the first kind (*II, 1*), by which work is conceived to be produced without consuming energy of any form. The law that perpetual motion of the second kind is impossible will be called the *perpetual-motion principle*.

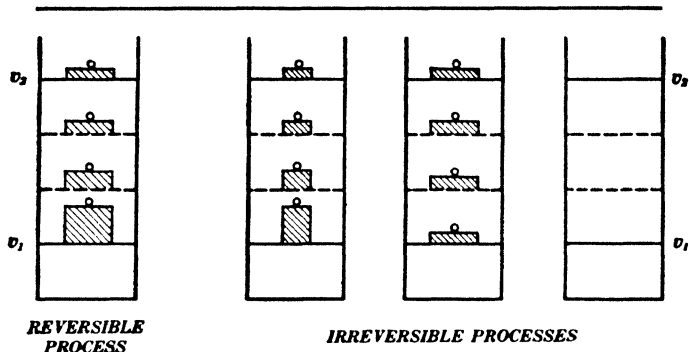
The perpetual-motion principle is a partial statement of a still more general law, known as the *second law of thermodynamics*, which applies also to the production of work out of heat by processes taking place at two or more temperatures. In its broader aspects this law will be later considered (*II, 26*). Here will be described the characteristics of a particular type of process known as a reversible process; and then there will be presented (*II, 18-21*) certain important principles relating to isothermal changes in state derivable from the perpetual-motion principle.

17. Reversible Processes of Bringing About Isothermal Changes in the Volume of Systems. — It has already been shown (II, 3) that a process of expansion produces the maximum work which the process is capable of producing in case the applied pressure is kept throughout the process substantially equal to the pressure exerted by the system, these two pressures differing always only by the infinitesimal amount which in the absence of friction suffices to cause the change in state to take place. It will now be shown that an expansion which takes place by a process that produces the maximum work can be made to take place in the opposite direction with the aid of that work alone, without withdrawing from the surroundings any additional work; and therefore that a process that produces the maximum work is also a process that is completely *reversible* in the sense that both the system and its surroundings can be restored to their original condition simply by reversing the process.

For explicitness, consider a *system* composed of one mol of some definite gas contained in a vertical cylinder closed by a weightless piston. Consider that the cylinder is immersed in *surroundings* of practically infinite heat-capacity at some definite temperature, and that these surroundings contain weights whose location at different levels determines the quantity of *work* existing in the surroundings. Consider that the gas undergoes a definite *change in state*, namely, a finite increase in volume (from v_1 to v_2) at the constant temperature of the surroundings, but that this change is brought about by a number of alternative *processes*, which differ in the respect that the piston is loaded to different extents with weights (belonging to the surroundings). Assume that there is a vacuum above the pistons, so as to avoid the complication of the pressure that would be exerted by the atmosphere. These considerations are illustrated by Fig. 3, on the next page.

Consider first that the process is one in which the piston moves without friction, and that the weight upon it is so adjusted during the expansion that the piston always exerts on the gas a pressure only infinitesimally less than that of the gas itself; an infinitesimal fraction of the weight being removed at each successive infinitesimally higher level. See the first sketch in Fig. 3, which shows, however, besides the initial and final volumes v_1 and v_2 , only two intermediate states, not an infinite series of them.

FIGURE 3. REVERSIBLE AND IRREVERSIBLE PROCESSES.



The pressure applied in this process is clearly the maximum pressure against which the expansion can conceivably take place; and the work produced in the surroundings (that corresponding to the raising of the weight) is therefore the maximum work which can be produced by the expansion of the gas, as previously shown (II, 3). The further fact is now to be noted that, when the expansion is carried out in this ideal way, under conditions of substantial balance between the externally applied pressure and the pressure exerted by the gas, the work produced in the surroundings is equal (within an infinitesimal amount) to that required to compress the gas to its original volume; for in this compression there need be applied at each stage a pressure greater only by an infinitesimal amount than that exerted by the gas and than that actually applied during its expansion. Hence, after the compression has taken place, not only has the gas been restored to its initial state, but the weights in the surroundings have been returned to their original levels. The original process of expansion has therefore been reversed in its entirety.

Consider secondly that the gas be expanded by processes in which, because of the necessity of overcoming friction or because of neglect to balance the pressures, the pressure applied on the piston is always less by a finite amount than that of the gas. Such processes are illustrated by the second, third, and fourth sketches in Fig. 3. In the second process the applied

pressure is kept always equal to two-thirds of the pressure which the gas has at each infinitesimal stage of its expansion; in the third process the applied pressure is kept constant at a value equal to the final pressure of the gas; and in the fourth process, constituting a limiting case, no external pressure is applied, so that no work whatever is produced.*

It is obvious that in each of these three processes less weight is raised, and therefore less work is produced in the surroundings, than in the process represented by the first sketch; and therefore that the maximum work ideally possible has not been produced. Yet, in order to compress the gas to its original volume, there would have to be placed upon the piston such weights as would keep the applied pressure greater by at least an infinitesimal amount than the pressure of the gas; and the result, after the gas was restored to its initial state, would be that weights in the surroundings would be at lower levels than they were originally, so that a net quantity of work would have disappeared in the surroundings and the original process of expansion would not have been reversed in its entirety.

Prob. 47. — Work Produced by Reversible and Irreversible Processes of Bringing About the Same Change in State. — a. Calculate the work in joules produced by each of the four processes represented by Fig. 3, assuming that the system consists of one mol of a perfect gas, that its initial and final volumes are 25 l. and 100 l., and that the temperature is 27°. *b.* Consider now that the gas, after it has expanded by each of the four processes, is brought back to its initial state by subjecting it to a compression process which is the opposite of the first expansion process illustrated in Fig. 3; and find and tabulate the quantity of work taken from the surroundings as the net result of the expansion and compression in each of the four cases.

In general, a process, like the first one sketched in Fig. 3, which is of such a character that the system can be restored to its initial state without producing any resultant change in the

* The fourth process illustrates clearly the distinction previously mentioned (II, 2) between the use of the term work in the science of mechanics and its use in the science of thermodynamics. For in a thermodynamic sense there is *no work produced* in the surroundings, since there results no change in the level of the weight in the surroundings; whereas in a mechanical sense there is *work done* by the gas in overcoming the friction of the piston.

conditions that originally existed in the surroundings, is called a *reversible process*. This is the definition or *criterion of reversibility*.

This primary criterion is satisfied, however, only when various *secondary conditions of reversibility* are fulfilled. These will be described as occasion requires. One of the most obvious of them may be now stated, as follows:

(1) In case the change in state is one that can produce work, the process must produce in the surroundings as large a quantity of work as suffices to cause the change in state to take place in the opposite direction; and therefore, if the process be one of expansion, the change must take place against an applied pressure only infinitesimally less than that of the system.

(2) In case the change in state is one that must consume work, the process must withdraw from the surroundings no greater quantity of work than can be restored to them by causing the change in state to take place in the opposite direction; and therefore, if the process be one of compression, the change must take place under an applied pressure only infinitesimally greater than that of the system.

A process, like any of the last three sketched in Fig. 3, which does not satisfy the criterion or secondary conditions of reversibility is called an irreversible process. That is, an *irreversible process* is one of such a character that, after it has taken place, the system and surroundings can not both be restored to their original conditions; or it is a process that produces less work in the surroundings than is required to restore the system to its initial state, or withdraws more work from the surroundings than can be produced in them by the return of the system to its initial state; or it is a process which produces less than the maximum work that can be produced, or consumes more than the minimum work that is required; or it is a process that takes place under an applied pressure less by a finite amount than that which the system can overcome, or under an applied pressure greater by a finite amount than that which suffices to cause the change in the system to take place.

The maximum work that can be produced by a definite type of process or the minimum work that must be consumed by a definite type of process, which is the quantity of work

involved when the process is reversible, may be called for short the *reversible work*, W_R .

The maximum work that can be produced, or the minimum work that must be consumed, has thus far been considered with respect to a definite type of process, not with respect to the change of state in the system thereby brought about. Yet the two things are not identical; for it is conceivable that a system in which a definite change in state had been produced by a reversible process of one type (say by a mechanical process) could be restored to its initial state by a reversible process of a different type (say by an electrical one) which consumes less work than does the reversal of the process of the first type. However, it will be shown later (II, 21) that the existence of any such more efficient process would be a contradiction of the perpetual-motion principle itself; and therefore that the maximum work that can be produced in the surroundings or the minimum work that must be withdrawn from them is a quantity determined by the change in state of the system, independent of the type of reversible process by which the change may be brought about.

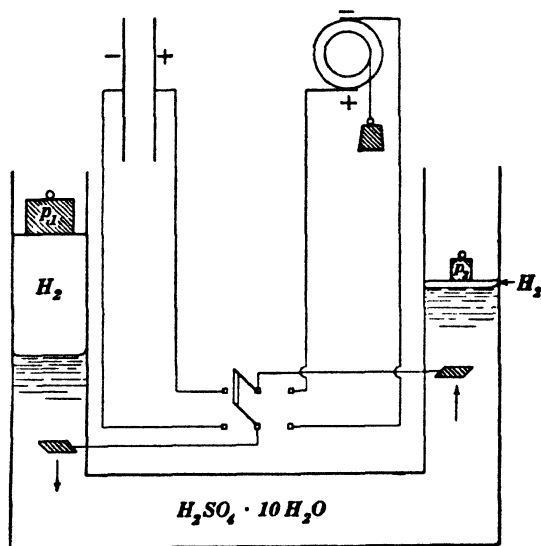
18. Reversible Electrical Processes of Bringing About Physical Changes in Systems. — The only type of reversible process thus far considered is that in which a system undergoes a change in volume against a pressure equal to its own equilibrium pressure. Many changes in state can also be brought about by reversible electrical processes. The production of work by such processes, which is of great importance in the study of chemical principles, will be discussed in some detail at this point because the presentation of the second law of thermodynamics is made clearer by applying it to two different types of processes.

An arrangement of matter that produces in the form of electrical energy the work which can be obtained from a physical or chemical change in the state of a system is called a *voltaic cell*, or often a galvanic cell. In order, however, that the work so produced may be stored in the surroundings, the voltaic cell must be supplemented by some other device, for example, by an electric condenser which stores the electrical energy as such, by a direct-current motor which transforms it into gravitational energy or compression energy, or by a storage cell which converts it into chemical energy.

Such an arrangement can best be illustrated by considering the following concrete example. Suppose it be desired to

produce by an electrical process the work which can be obtained when a system composed of N mols of hydrogen changes at a temperature T from an initial state where its pressure and volume are p_1 and v_1 to a final state where its pressure and volume are p_2 and v_2 , the pressure p_1 being larger than the pressure p_2 . Such an electrical process can be realized with the aid of a voltaic cell connected with an electric condenser or with a direct-current motor arranged as shown in Fig. 4.

FIGURE 4. AN ELECTRICAL REVERSIBLE PROCESS.



In the left arm of the cell are the N mols of hydrogen under a piston loaded with a weight that exerts upon the gas the (initial) pressure p_1 . Beneath this hydrogen is aqueous sulfuric acid, which fills the lower part of the vessel. Above this acid in the right arm is an infinitesimal layer (dN mols) of hydrogen under a piston loaded with a weight that exerts upon the gas a pressure p_2 , equal to the final pressure to which the hydrogen is to be brought. In each arm, below the surface of the sulfuric acid, which is saturated with hydrogen gas at its prevailing pressure (p_1 or p_2), is inserted a platinum electrode, whose surface likewise becomes saturated with hydrogen, making it in effect a hydrogen electrode. This cell is found to produce an *electro-*

motive force $\mathcal{E}$ (a tendency to drive positive electricity) in the direction of the arrows, of a magnitude that depends on the two hydrogen pressures. The two electrodes are connected, either with the metal plates of an electric condenser of practically infinite capacity (shown above at the left), or with the terminals of a direct-current motor (shown above at the right) loaded with a suitable weight.* The plates of the condenser are already charged with (equal) quantities of positive and of negative electricity (shown by the + and - signs†) sufficient to cause the condenser to have an electromotive force $\mathcal{E}$ equal and opposite to that produced by the voltaic cell; or the motor is rotating at such a speed as to generate an electromotive force of this direction and magnitude.

The voltaic cell is placed in a heat-reservoir of practically infinite heat-capacity at a uniform temperature T ; and this reservoir, the weights on the pistons, and the condenser with its electrical charge or the motor with the weight at a certain level constitute the surroundings where the work and heat effects occur.

Now by decreasing the pressure p_1 on the dN mol of hydrogen in the right arm of the cell by the infinitesimal amount dp_1 , the electromotive force $\mathcal{E}$ produced by the cell will become greater by an infinitesimal amount $d\mathcal{E}$ than the counter electromotive force $\mathcal{E}$ of the condenser or motor, and positive electricity will flow through the cell to the positive plate of the condenser or into the motor, thereby transferring hydrogen from one electrode to another. This is continued until the N mols of hydrogen gas have disappeared from the left arm of the cell at the pressure p_1 and have appeared in the right arm of the cell at pressure p_2 , thereby bringing about the desired change in state.

* The condenser is simpler in principle, since it stores as such the electrical work directly produced by the voltaic cell; but in practice a condenser would have to be of enormous extent to store at the small potentials of voltaic cells the quantity of electricity attending the voltaic action that involves even one equivalent of substance. The condenser is considered to be of infinite capacity, not only for this reason, but also in order that its electromotive force may change only infinitesimally when its charge is increased by a finite amount. The motor serves to change the electrical work produced by the voltaic cell immediately into mechanical work, for example into gravitational energy by raising a weight.

† Note that + and - signs are used here to represent charges of positive and negative electricity, not the direction of the resultant electromotive force, which is varied according to the direction in which the voltaic process is to take place.

The molecular and ionic mechanisms by which the cell produces this result will be later discussed in detail. Here they will be only briefly indicated, since they are not essential to the thermodynamic interpretation. At the left-hand side of the cell the neutral hydrogen molecules pass from the gas phase into the solution, and at the electrode break up into atoms and give off their electrons, becoming hydrogen ions (H^+), which migrate through the solution; and at the right-hand electrode the hydrogen ions in the solution take up electrons and become neutral hydrogen atoms which unite to form hydrogen molecules, and these escape from the solution into the gas phase.

Of great importance is the fact that in principle this process can be made directly reversible. For, after transfer of the hydrogen to the smaller pressure p_2 has taken place, by increasing the pressure on this hydrogen by the infinitesimal amount dp_2 , the electromotive force E produced by the cell will be decreased by an infinitesimal amount dE , an infinitesimal current will flow from the condenser or motor through the cell in the opposite direction, and the hydrogen will pass back into the left arm of the cell where its pressure is p_1 . The result is evidently that the system has returned to its initial state without withdrawing from the condenser or motor a larger quantity of electricity or of electrical energy than was originally delivered to it; so that the surroundings have also been restored to their original condition.

Processes taking place in voltaic cells would be irreversible in case heat were produced as a result of the electric resistance to the flow of the current. In thermodynamic derivations this is avoided by considering the potential-difference and the resulting current to be infinitesimal. Under these conditions the heat produced is also infinitesimal and the loss of work by its conversion into heat is negligible. This follows from *Joule's law*, $Q = I^2 R t$, which expresses the heat Q produced when a current I passes for time t through a resistance R . Noting that the product $I t$ represents the quantity of electricity that is passed, this expression evidently shows that the heat produced when a specified quantity of electricity passes through a definite resistance is proportional to the current, so that the heat and the current become infinitesimal together.

Before evaluating the work obtainable by this process, expressions for the work produced by reversible voltaic processes in general will be derived. This may be done as follows. It is a basic energy principle that, when a quantity of positive electricity

q is transferred from a place where the electric potential is v_1 to a place where the electric potential is v_2 , or is transferred against an *electromotive force* E (defined to be equal to the potential-difference $v_2 - v_1$), the quantity of electrical work W_{el} produced is given by the expression:

$$W_{\text{el}} = (v_2 - v_1)q = E q. \quad (31)$$

Now it will be seen later (Chap. V) that there is a fundamental law of electrochemistry, known as *Faraday's law*, which states that the quantity of electricity q flowing through a voltaic cell is strictly proportional to the number N_{eq} of oxidation-equivalents ($I, 9$) of chemical substance that are involved in the chemical change at each electrode. To formulate this law one may introduce a constant F denoting the quantity of electricity, called one *faraday* and found equal to 96 500 coulombs, which passes through any cell when a chemical change that involves one equivalent takes place at each electrode; and one may represent by n the number of faradays passing through a given cell in any given case. Then the quantity of electricity q flowing through this cell will be equal to nF coulombs; Faraday's law will be expressed by the equation $n = N_{\text{eq}}$, where N_{eq} denotes the number of equivalents of substance which undergo oxidation or reduction at each electrode; and the maximum electrical work that can be obtained, in case the tendency of this change in state to take place produces in the cell an electromotive force E , will be given by the expression:

$$W_{\text{el}} = n E F. \quad (32)$$

Since a voltaic cell ordinarily produces a quantity of mechanical work corresponding to the volume-increments ($v_2' - v_1'$; $v_2'' - v_1''$; ...) that take place in the different parts of the cell under their respective pressures (p' , p'' , ...), the general expression for the maximum work W_{r} obtainable from any definite change in state that can be brought about reversibly in a voltaic cell is as follows:

$$\begin{aligned} W_{\text{r}} &= n E F + p'(v_2' - v_1') + p''(v_2'' - v_1'') + \dots \\ &= n E F + \Sigma(p \Delta v). \end{aligned} \quad (33)$$

This result applied to the change in pressure and volume from p_1 and v_1 to p_2 and v_2 of the N mols of hydrogen gas (equal to $2N$ equivalents) by the voltaic process considered above evidently gives for the maximum work attending that process the expression:

$$W_R = 2N E F + p_2 v_2 - p_1 v_1. \quad (34)$$

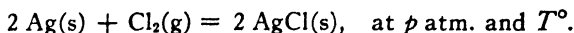
19. Reversible Electrical Processes of Bringing About Chemical Changes in Systems. — Chemical changes, as well as physical changes, may be brought about in voltaic cells by reversible electrical processes, as will be now illustrated. Eq. 33 shows that the total work W_R produced by a voltaic cell which operates reversibly at a constant pressure p and at a constant temperature and produces an electromotive force E is given by the following expression, in which $N F$ represents the coulombs of electricity passed through and Δv the attendant increase in the volume of the substances constituting the cell:

$$W_R = N E F + p \Delta v. \quad (35)$$

This equation evidently makes it possible to derive from electromotive force measurements the work producible by chemical changes (occurring at constant temperature and pressure), provided the change under consideration can be made to take place reversibly in a voltaic cell. However, in order that a voltaic process may be reversible in its entirety and thus fulfil the criterion of reversibility (II, 17), it is essential, not only that the electromotive force produced by the cell be counterbalanced by a substantially equal applied electromotive force (as in the process of Fig. 4), but also that the observed electromotive force of the cell arise strictly from the chemical change under consideration, so that this particular chemical change takes place in opposite directions when the counterbalancing electromotive force is infinitesimally varied. This last is evidently another necessary *condition of reversibility*, applicable to voltaic processes.

Prob. 48. — Reversible Electrical Processes of Bringing About Chemical Changes. — Consider a voltaic cell made by partially filling a vertical cylinder with 0.1 f. HCl solution, inserting at the bottom an electrode of silver covered with silver chloride and at the top of the solution an electrode consisting of an inert metal M, such as iridium, and placing above the solution chlorine

gas under a piston on which a pressure of p atm. is exerted, as represented by the formulation $\text{Ag(s)} + \text{AgCl(s)}, \text{HCl(0.1 f.)}, \text{Cl}_2(\text{g}, p \text{ atm.}) + \text{M}$. Such a cell produces at any definite temperature T a definite electromotive force E ; and when 2 faradays of electricity are passed through the cell from left to right there takes place in it the change in state:



- a. State the conditions under which the process would be reversible.
- b. Find the exact value in joules of the electrical work produced when under reversible conditions two faradays pass through a cell of this type at 25° and 1 atm., at which temperature and pressure its electromotive force is $+1.136$ volts.
- c. For the same process calculate an approximate value of the expansion-work and of the total work, neglecting the volumes of the solid silver and solid silver chloride and considering the chlorine to be a perfect gas.

20. Reversible Expansion Processes of Bringing About Chemical Changes in Systems.—It has just been seen that chemical changes in systems can sometimes be brought about reversibly in voltaic cells, with the production of electrical work. Chemical changes can be brought about also by reversible processes that involve only expansion work. Such processes are very fully treated in a later chapter. They are here considered in a preliminary way only for the purposes of further illustrating the application of general thermodynamic principles and of indicating their great importance in chemical considerations.

One new *condition of reversibility* (II, 17) may first be noted. Namely, in order to make reversible an expansion process involving a chemical reaction, not only must the pressure of the system be balanced by an equal applied pressure, but also this pressure must be that at which chemical equilibrium prevails within the system; for, otherwise, the change in state under consideration will not take place in the opposite direction when the external pressure is varied by an infinitesimal amount.

Prob. 49. — Additional Necessary Condition of Reversibility in the Case of Expansion Processes of Bringing About Chemical Changes.—Consider a system consisting of metallic silver, solid silver oxide (Ag_2O), and gaseous oxygen contained in a vessel closed with a weighted frictionless piston, the whole being placed in surroundings at 200° . Take into account the facts that at 200° silver oxide may dissociate into silver and oxygen in accordance

with the equation $2\text{Ag}_2\text{O}(\text{s}) = 4\text{Ag}(\text{s}) + \text{O}_2(\text{g})$ when the pressure is less than 1.36 atm., but that the opposite reaction can take place only when the pressure is greater than 1.36 atm. *a.* Explain in what respect the primary criterion of reversibility (II, 17) is not fulfilled by the process that occurs when at 200° a pressure of 1 atm. is maintained on the piston and some of the silver oxide dissociates, even though the applied pressure and the actually prevailing pressure of the oxygen are kept substantially equal to one another at a value of 1 atm. (by steadily raising the piston as fast as a higher pressure tends to develop). *b.* Describe a process by which at 200° silver oxide can be reversibly dissociated into metallic silver and gaseous oxygen.

Prob. 50. — Reversible Expansion Processes of Bringing About the Dissociation of Substances. — Consider the following isothermal reversible process of bringing about at 200° the change in state $2\text{Ag}_2\text{O}(\text{s}) (p_1 \text{ atm.}) = 4\text{Ag}(\text{s}) (p_2 \text{ atm.}) + \text{O}_2(\text{g}) (p_2 \text{ atm.})$ for the case that the initial and final pressures p_1 and p_2 are equal to two and one atmospheres, respectively.

(1) Starting with $2\text{Ag}_2\text{O}(\text{s})$ in a cylinder under a frictionless piston exerting a pressure of p_1 (2 atm.), expand the silver oxide by reversibly increasing the pressure till it becomes equal to the dissociation-pressure p (1.36 atm.) at which silver oxide, silver, and oxygen are in equilibrium at 200° .

(2) Decrease the pressure p on the silver oxide by an infinitesimal amount so as to cause it to decompose into silver and oxygen gas of volume v under this constant pressure.

(3) Expand the silver and oxygen gas by reversibly decreasing the pressure from substantially the dissociation pressure p (1.36 atm.), till it attains the final value p_2 (1 atm.), whereby the oxygen gas assumes a volume v_2 .

a. Neglecting the small quantities of work attending the small changes in volume of the solid silver oxide and the metallic silver, formulate an algebraic expression in terms of the pressures and volumes for the work W_R produced by the whole process. *b.* Considering the oxygen to be a perfect gas integrate the expression and evaluate the work in calories.

21. Work Producing from the Same Change in State by Different Reversible Processes. — It has already been shown (II, 17) that any specified change in state produces a definite quantity of work when the change in state is brought about by a directly reversible process of any definite type. It will now be shown that the perpetual-motion principle requires that the quantity of work attending an isothermal change in state is the same, whatever be the type of reversible process by which the

change be brought about. For in case two reversible processes I and II of different types, say a mechanical process and an electrical process, in bringing about the same isothermal change of state could produce unequal quantities of work W_I and W_{II} , then, by causing the change in state to take place by the process producing the larger quantity of work (say, process II) and restoring the system to its initial state by the process attended by the smaller quantity of work (process I), a quantity of work $W_{II} - W_I$ would be produced out of heat in the surroundings without any resultant change in the state of the system. Since by repeating this cycle of operations an unlimited quantity of work could be produced, perpetual motion of the second kind would have been realized. This work is assumed to be produced out of heat in the surroundings so that the result may be no contradiction of the first law of thermodynamics; but it would, nevertheless, be incompatible with the second law.

For example, consider that a system composed of N mols of hydrogen in the condition of a perfect gas undergoes in surroundings at constant temperature T a change from an initial state in which its pressure is p_1 and its volume v_1 to a final state in which its pressure is p_2 and its volume v_2 . Consider further that this change in state is brought about successively by two directly reversible processes of different types; namely, in one case by a reversible process (process I) that consists of expansion (or compression) of the gas in a cylinder with a frictionless weighted piston, and in another case by a reversible process (process II) that employs a voltaic cell for producing electrical work, like that shown in Fig. 4 (II, 18). Note now that the work W_I that attends the first (expansion) process of changing the pressure of the hydrogen gas from p_1 to p_2 at the temperature T is the maximum work that attends the direct isothermal expansion of a perfect gas, which has already been shown (Eq. 8; II, 3) to be $NR T \ln (p_1/p_2)$; and that the work W_{II} attending the second (electrical) process was shown (Eq. 34; II, 18) to be $2N e F + p_2 v_2 - p_1 v_1$; also that, since the hydrogen is now considered to be a perfect gas, the difference of the two $p v$ products is zero. But these two quantities of work W_I and W_{II} attending these two different types of directly reversible processes of bringing about the same change in state must be equal, as shown

above, since otherwise perpetual motion of the second kind could be realized. Therefore,

$$R T \ln (p_1/p_2) = 2 E F.$$

Prob. 51. — Electromotive Force of a Gas Concentration Cell. — Calculate the electromotive force in volts produced at 27° by a cell like that shown in Fig. 4 with pressures of 1.0 and 0.1 atm.

Note. — This example illustrates not only the fundamental thermodynamic principle under consideration, but also the general character of the physico-chemical relations that can be derived with its aid; thus the principle gives in this case a relation between the electromotive force of a type of voltaic cell and the pressures of the gas at its two electrodes.

*** Prob. 52. — Equilibrium-Pressure of a Reaction Derived from the Electromotive Force of a Voltaic Cell.* — With the aid of the here-considered principle and of the principles relating to expansion processes of bringing about chemical changes (Prob. 50; II, 20) derive from the electromotive force, 1.136 volts, of the cell $\text{Ag(s)} + \text{AgCl(s)}, \text{HCl(0.1 f.)}, \text{Cl}_2(\text{g}, 1 \text{ atm})$ at 25° (considered in Prob. 48) the (very small) value of the equilibrium-pressure of the reaction $2\text{Ag(s)} + \text{Cl}_2(\text{g}) = 2\text{AgCl(s)}$ at 25° .

An obvious consequence of the above considered principle stating the equality of the quantities of work obtainable from the same change in state by different reversible processes is expressed by the following statement: When a system goes through a cycle (II, 16) of isothermal changes, each of which is brought about by a reversible process, the algebraic sum of all the separate quantities of work produced is zero. That is, for a cycle of isothermal changes,

$$\Sigma W_n = 0. \quad (36)$$

For example, if 1 mol of hydrogen in the state of a perfect gas were changed at temperature T in pressure and volume from p_1 and v_1 to p_2 and v_2 by the reversible electrical process above described, and if the gas were then restored to the initial pressure and volume by a reversible compression process, the algebraic sum of the two quantities of work produced would be zero; that is,

$$2 E F - R T \ln (p_1/p_2) = 0.$$

22. Concepts of Work-Content and of Free-Energy Content.— Since it was shown (II, 21) that a definite isothermal

change in the state of a system that takes place of itself (that is, without utilizing work in the surroundings) is capable of producing a perfectly definite quantity of work (a quantity which is never exceeded, whatever be the process by which the change in state takes place), it is to be inferred that a system in any definite state possesses a certain *power of producing work* (Helmholtz, 1882),* which may be briefly named its *work-content* A . This implies also that this property changes by some definite amount (from A_1 to A_2) when the system undergoes any definite change in state, whatever be the process by which this change takes place, and whatever be the quantity of work which is actually produced. For example, N mols of oxygen gas at any temperature T possesses a certain power of producing work or a certain work-content A_1 when at a pressure p_1 and volume v_1 , and a certain smaller power of producing work or smaller work-content A_2 after the oxygen has expanded so that its pressure is p_2 and its volume v_2 , whether or not this expansion has been brought about by a process that actually produces an amount of work equal to the loss in work-content. In other words, the work-content of a system is a quantity characteristic of its state: it is another thermodynamic property of a system, like its energy-content or heat-content, which changes in value, when a change in its state takes place, by an amount that is determined solely by the initial state and the final state of the system. The concept of work-content and the related concept of free energy described below are, as here presented, limited to changes in state at a constant temperature. This limitation is removed by more general definition of these properties to be given later (II, 29).

In the case of any isothermal change in state, the difference $A_1 - A_2$, obtained by subtracting from the work-content A_1 of the system in its initial state (state 1) its work-content A_2 in its final state (state 2), whether the numerical value of this difference be positive or negative, is called the *decrease in work-content* ($-\Delta A$). The decrease in work-content is evidently equal to the maximum work which the change in state can produce, or

* Helmholtz called this quantity the *free-energy* of the system — a name now applied to a somewhat different quantity defined below and denoted by F , not A . Closely related functions had previously been used by others (especially by Gibbs, 1873).

to the work W_R which the change actually produces when it is brought about by any reversible process. That is, for any isothermal change in state,

$$A_1 - A_2 = -\Delta A = W_R. \quad (37)$$

To determine the work-content decrease for a given change in state, it is necessary, in accordance with these principles, to find a reversible process by which that change may be brought about and to evaluate the work which such a process produces. To illustrate this, consider the change in state of N mols of oxygen at T from the state p_1 and v_1 to the state p_2 and v_2 for the case where the pressures are so small that the gas may be considered perfect. A reversible process for bringing about such changes has been described, and it has been shown (Eq. 8; II, 3) that for this process $W_R = N R T \ln (p_1/p_2)$. Therefore it follows that for this change in state $-\Delta A = N R T \ln (p_1/p_2)$.

It will be noted that, although the first law of thermodynamics requires that there be a quantity of energy produced in the surroundings equal to the decrease of the energy-content of the system, yet the second law does not require that there be a quantity of work produced equal to the decrease in work-content. The second law requires only that the quantity of work W actually produced be not greater than the decrease in work-content. That is, for any isothermal change in the state of a system,

$$W > -\Delta A, \quad \text{for no process whatever.}$$

$$W = -\Delta A, \quad \text{for a reversible process.}$$

$$W < -\Delta A, \quad \text{for an irreversible process.}$$

Just as it is usually more convenient to consider the heat-content rather than the energy-content of systems, so there are many advantages in considering in place of the work-content a quantity which differs from it, just as heat-content differs from energy-content, by the value of the pressure-volume product of the system (*G. N. Lewis, 1899*). This quantity, which is called the *free-energy content* of the system, or often simply its *free energy*, is defined by the equation:

$$F = A + p v. \quad (38)$$

The value of the free energy F of a system is evidently determined by its state, since the values of its work-content A and of its pressure-volume product $p v$ are so determined; and the value of the *decrease in free energy*, $F_1 - F_2$, or $-\Delta F$, that attends an isothermal change in the system from an initial state (state 1) to a final state (state 2) is evidently equal to the work W_{R} produced when that change takes place by a reversible process, diminished by the increase of the pressure-volume product. That is, for any isothermal change in the state of a system:

$$F_1 - F_2 = W_{\text{R}} - (p_2 v_2 - p_1 v_1); \text{ or } -\Delta F = W_{\text{R}} - \Delta(pv). \quad (39)$$

The above expressions and some other principles relating to work-content and to free-energy content are formulated in Table III, which is similar to Table I (II, 6), with which it should be compared. It is, however, to be noted that the expressions of Table III are subject to two limitations not applicable to those of Table I; namely, to the limitations that the change in state and the processes bringing them about be isothermal and that the processes be reversible. These expressions are illustrated below (II, 23, 24) by applying them to important types of physical and chemical changes.

Note especially the new relations $-dA = p dv$ and $-dF = -v dp$, and the contrast between them.

TABLE III. GENERAL EXPRESSIONS FOR THE DECREASE IN WORK-CONTENT AND IN FREE-ENERGY CONTENT ATTENDING ISOTHERMAL CHANGES.

<i>Applicable to</i>	<i>In Terms of Work-Content</i>	<i>In Terms of Free Energy</i>
Any infinitesimal change in state	$-dA$	$-dF = -dA - d(pv)$
Any infinitesimal reversible process	$-dA = dW_{\text{R}}$	$-dF = dW_{\text{R}} - d(pv)$
Any finite reversible process	$A_1 - A_2 = W_{\text{R}}$	$F_1 - F_2 = W_{\text{R}} - (p_2 v_2 - p_1 v_1)$
An infinitesimal reversible process involving no work except expansion work	$-dA = p dv$	$-dF = -v dp$
A finite reversible process at constant pressure involving no work except expansion work	$A_1 - A_2 = p(v_2 - v_1)$	$F_1 - F_2 = 0$

Prob. 53. — Derivation of Expressions for Free-Energy Decreases. — Derive each of the free-energy expressions given in Table III from the relationship determining work-content decrease (Eq. 37), the definition of free energy (Eq. 38), and the expression for the maximum work attending volume changes (Eq. 4; II, 3).

**** General Definitions of Heat-Content and Free-Energy Content.**

In cases where different phases of the system, having different volumes $v', v'', v''', \dots$, are subjected to different pressures $p', p'', p''', \dots$ the above-given definition of free energy and that given earlier (II, 6) for heat-content, by the equations $F = A + p v$ and $H = E + p v$, are obviously inadequate. For the general case, where different parts of the system have different pressures, these properties are defined by the equations:

$$F = A + p' v' + p'' v'' + \dots = A + \Sigma(pv);$$

$$\text{and } -\Delta F = -\Delta A - \Delta \Sigma(pv). \quad (40)$$

$$H = E + p' v' + p'' v'' + \dots = E + \Sigma(pv);$$

$$\text{and } \Delta H = \Delta E + \Delta \Sigma(pv). \quad (41)$$

An example of a change to which these more general definitions must be applied is that of the voltaic cell of Fig. 4 (II, 18), in which the hydrogen undergoes a change of its pressure-volume product in one arm from $p_1 v_1$ to zero and in the other arm from zero to $p_2 v_2$, so that $-\Delta \Sigma(pv) = p_1 v_1 - p_2 v_2$ for the system.

23. Decrease in Free Energy Attending Isothermal Physical Changes. — A knowledge of the free-energy decrease attending changes in the physical and chemical states of systems is of great assistance in deriving relations between the physical properties of substances, in determining the equilibrium conditions of chemical reactions, and in evaluating the electromotive force of voltaic cells. Expressions for the free-energy decrease that attends some important types of physical changes are derived in the following problems.

Free-Energy Decrease Attending Volume Changes.

Prob. 54. — Expansion of Perfect Gases. — *a.* Derive an expression for the decrease in the free energy that attends a change in the pressure and volume of N mols of a perfect gas from p_1 and v_1 to p_2 and v_2 at temperature T . *b.* Formulate expressions for the changes in work-content, energy-content, and heat-content that attend the same change in state.

**** Prob. 55. — Expansion of Imperfect Gases at Moderate Pressures.** — Up to moderate pressures (so long as the deviation from the perfect-gas equation does not exceed a few percent) the pressure-volume relations of gases at any definite temperature are expressed (*III, 4*) by the equation of state $p v (1 - \beta p) = N R T$, in which β is a coefficient depending on the nature of the gas and on the temperature. *a.* Derive an expression for the free-energy decrease attending the change in the pressure of N mols of such a gas from p_1 to p_2 at temperature T . *b.* Find the free-energy decrease in calories attending the expansion of 16 g. of oxygen at 0° from 10 atm. to 1 atm., for which case the value of β is -0.00094 .

**** Prob. 56. — Compression of Liquids.** — Calculate the free-energy decrease attending the compression of 1 $\text{C}_2\text{H}_5\text{OH}(\text{l})$ at 20° from 1 atm. to 25 atm., assuming the equation of state (*I, 13*), $v = v_0 (1 - \beta p)$, where $\beta = 0.000105$ when the pressure-unit is the atmosphere. Its density at 20° and 1 atm. is 0.789 g./ml.

Note. — The smallness of this free-energy decrease compared with that found in Prob. 55b illustrates the fact that, except in precise calculations, the free-energy changes attending volume-changes of liquids or solids can be neglected when gases with their much larger volume-changes are involved.

Free-Energy Decrease Attending Changes in Aggregation-State.

Prob. 57. — Effects when the Final and Initial States are in Equilibrium. — *a, b.* Give the values in calories of the decreases in work-content, in free energy, and in heat-content that attend the change in state described, *a*, in Prob. 1a (*II, 3*); *b*, in Prob. 2 (*II, 3*). *c.* State what these decreases would be if 1 $\text{H}_2\text{O}(\text{l})$ at 100° and 1 atm. were changed to 1 $\text{H}_2\text{O}(\text{g})$ at 100° and 1 atm. by a process that produced no work, for example, by introducing the liquid water into an evacuated vessel having a volume equal to that of the vapor at 100° and 1 atm.

Prob. 58. — Effects when the Final and Initial States are Not in Equilibrium. — *a.* Devise and describe in detail a three-step isothermal process that is reversible at every stage by which 1 $\text{H}_2\text{O}(\text{l})$ at -5° and 3.163 mm. (equal to its vapor-pressure) could be converted into 1 $\text{H}_2\text{O}(\text{s})$ at -5° and at 3.013 mm. (equal to its vapor-pressure). Note that at -5° and the specified pressures water and ice are not in equilibrium (*I, 17*), and that when placed in contact with each other the water rapidly changes to ice by an irreversible process; but note also that, taken separately, water at 3.163 mm. or ice at 3.013 mm. is at -5° in equilibrium with water vapor, and can be converted into it reversibly by the usual expansion process. *b.* Calculate the work-content decrease and free-energy decrease attending the change at -5° of 1 $\text{H}_2\text{O}(\text{l})$ at 3.163 mm. to 1 $\text{H}_2\text{O}(\text{s})$ at 3.013 mm.

The above derived expressions for the free-energy decrease attending volume changes are summarized for future reference in Table IV. These expressions refer to changes at a temperature T involving N mols or N_f formular weights of a substance having an initial pressure p_i and a final pressure p_s .

TABLE IV. FREE-ENERGY DECREASE ATTENDING VOLUME CHANGES.

<i>State of Substance</i>	<i>Equation of State</i>	<i>Free-Energy Decrease ($-\Delta F$)</i>
Perfect Gas	$p v = N R T$	$N R T \ln \frac{p_i}{p_s} \quad (42)$
Imperfect Gas	$p v (1 - \beta p) = N R T$	$N R T \ln \frac{p_i / (1 - \beta p_i)}{p_s / (1 - \beta p_s)} \quad (43)$
Liquid	$v = v_0 (1 - \beta p)$	$N_f v_0 (p_i - p_s) \left(1 - \beta \frac{p_s + p_i}{2} \right) \quad (44)$

It has also been seen (Prob. 58) that the free-energy decrease attending the transition of a pure solid phase whose vapor-pressure is p_i into a pure liquid phase or into another pure solid phase whose vapor-pressure is p_s is represented by Eq. 42 in case the vapor may be considered a perfect gas; and it would evidently be represented by Eq. 43 in case the vapor is an imperfect gas at moderate pressure.

This leads to two more general free-energy principles relating to the transition of liquid or solid phases; namely, one with respect to their equilibrium, which prevails when their vapor-pressures are equal; and another with respect to the direction in which the transition tends to take place, which evidently must be the direction which is attended by a decrease in the vapor-pressure (II, 25). These general principles may be stated as follows:

(1) The decrease in free energy (but not the decrease in work-content) is zero for any isothermal change in the state of aggregation of a pure substance, such as the vaporization of a liquid or the fusion, sublimation, or crystalline transition of a solid, at the temperature and pressure at which the two phases are in equilibrium; and conversely.

(2) In case two different phases of a pure substance are not in equilibrium, the decrease in free energy has a positive value

when the substance undergoes a change in its aggregation-state in that direction in which the change takes place of itself; and conversely. For example, this is true when at -5° liquid water changes to ice. (By taking place *of itself* is meant here, as always, taking place within the system, without being caused by influences from the surroundings.) In other words, the more *stable state* is that in which the substance has the smaller free-energy content.

It will be seen later that these are general criteria for determining whether equilibrium prevails within an isothermal system and for predicting the direction in which a change within an isothermal system can take place of itself; thus they are applicable also to chemical changes. Namely, for any change taking place under conditions which are substantially those at which equilibrium prevails within the system:

$$-\Delta F = 0. \quad (45)$$

And for any change in a system occurring in the direction in which the change takes place of itself:

$$-\Delta F > 0. \quad (46)$$

These general relations to the conditions of equilibrium are mentioned here, in advance of their detailed consideration, to indicate the enormous importance of free energy in chemical considerations.

24. Decrease in Free Energy Attending Isothermal Chemical Changes. — There are two general methods of determining the free-energy decrease attending chemical reactions, corresponding to the two types of reversible processes of bringing about chemical changes (*II*, 19, 20). These will later be very fully considered; but they will be outlined here, with the aid of specific examples, to illustrate further the free-energy concept and to emphasize thus early its importance in chemistry.

One of these methods is to measure the electromotive force of a voltaic cell in which the chemical reaction under consideration takes place reversibly. For example, in case it were desired to determine the free-energy decrease attending the combination at 25° and 1 atm. of metallic silver and gaseous chlorine, this could be done by causing the reaction to take place in a voltaic cell (as in Prob. 48; *II*, 19). In this process, which in-

volves both electrical work and expansion work, the expression for the maximum work was found to be $W_{\text{r}} = N E F + p \Delta v$. This is the expression also for the work-content decrease $-\Delta A$; but, since the increase in the pressure-volume product is $p \Delta v$, the free-energy decrease is expressed by the simpler equation:

$$-\Delta F = N E F. \quad (47)$$

It may be noted that this kind of simplification is frequent, and that it is one of the advantages which result from the use of free energy in place of maximum work or of work-content.

The second method of finding the free-energy decrease attending a chemical reaction uses an expansion process involving the conditions of equilibrium of the reaction. For example, in case it be desired to find the free-energy decrease attending the change $2\text{Ag}_2\text{O}(\text{s}) = 4\text{Ag}(\text{s}) + \text{O}_2(\text{g})$ at 1 atm., this may be done by employing the reversible expansion process which was described in detail in Prob. 50 (II, 20). Neglecting the expansion work attending the small changes in volume of the solid oxide and metal, the maximum work produced by the whole process was found to be given by the following expression (whose last member results from the preceding member in virtue of the mathematical relation $d(pv) = p dv + v dp$):

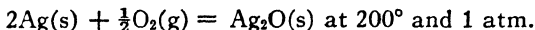
$$W_{\text{r}} = p v + \int_v^{v_2} p dv = p_2 v_2 + \int_{p_2}^p v dp.$$

This is the approximate expression also for the work-content decrease $-\Delta A$; but, since the increase in the pressure-volume product is $p_2 v_2$, the free-energy decrease is expressed by the equation:

$$-\Delta F = \int_{p_2}^p v dp = (\text{in case the gas be perfect}) N R T \ln \frac{p}{p_2}.$$

It will be noted that these expressions involve as variables besides the temperature only the pressure p at which the reaction is at equilibrium and the actual pressure p_2 at which the reaction is considered to take place and for which the attendant free-energy decrease is to be evaluated; thus in the case of the silver-oxide dissociation at 200° these pressures are 1.36 atm. and 1.0 atm., respectively.

Prob. 59. — Free-Energy Decrease Attending the Formation of a Solid Substance from Gaseous (and Solid) Products. — a. Derive the above-given expression by considering the free-energy decrease attending each step of the reversible process described in Prob. 50. *b.* Calculate from the data previously given (Probs. 48, 50) the free-energy decrease in calories attending the changes in state:



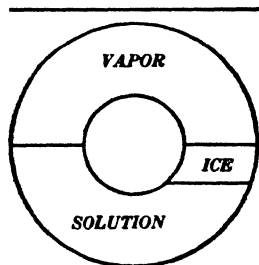
b. Explain what the result in each case shows as to the direction in which the change takes place of itself.

25. Thermodynamic Law of Equilibrium between Phases at the Same Temperature. — The impossibility of perpetual motion of the second kind leads to the following *law of phase equilibrium*, applicable to three or more phases coexisting at any definite temperature: When each of two phases is in equilibrium with the same third phase, the two phases are in equilibrium with each other, with respect to every substance present.

This law may be illustrated and derived in the following way, taking for definiteness a special case. Consider a system composed of water and a non-volatile salt (such as sodium chloride), at such a temperature that the system exists in the form of the three phases, solution, ice, and water-vapor (Fig. 5).

Assume now that the solution and the ice are in equilibrium and also that the ice and water-vapor are in equilibrium; which signifies (*I, 17*) that, however long the solution and the ice be in contact, ice can not melt into the solution or separate from the solution, and that, however long the ice and the vapor be in contact, ice can not change to vapor and water-vapor can not condense to ice. Then from the perpetual-motion principle it follows that the solution and the water-vapor must also be in equilibrium; that is, that, however long these be in contact, no water can vaporize from the solution and no water-vapor can condense into the solution. For, if water vaporized from the solution, this would increase the pressure of the water-vapor above the solution, the vapor would flow to the surface of the ice,

FIGURE 5. THREE-PHASE EQUILIBRIUM.



thereby increasing its pressure above the ice, and it would there condense to ice; but this ice would melt into the solution, since the solution, having been concentrated by the vaporization of the water, would no longer be in equilibrium with the ice. On the other hand, if water-vapor condensed into the solution, this would decrease the pressure of the water-vapor above the solution, and the converse processes would take place. In either case the result would be that the substance water would flow continuously through the system, and could be made to produce work in unlimited quantity, for example, by placing a windmill in the flowing vapor.

Inasmuch as the vapor-pressure of a substance in a liquid or solid phase is by definition (*I, 18*) equal to the pressure of the vapor of that substance at which equilibrium prevails between the liquid or solid phase and the gaseous phase, the law of phase equilibrium may be stated as follows. When a system is in equilibrium, the vapor-pressure of any substance present has the same value in every solid and liquid phase of the system. Thus, to cite a new example, the two crystalline forms of sulfur, the rhombic and monoclinic, are found to be in equilibrium with one another and with sulfur vapor at 95.5° , their transition-temperature; hence these two crystalline forms of sulfur must at this temperature have equal vapor-pressures.

This law of phase equilibrium may be stated more concisely, but less explicitly, as follows: What is in equilibrium in one way must be in equilibrium in every way (*Ostwald, 1890*). This statement of the law applied to the special case considered in the text, shows that, if the ice and vapor are in equilibrium directly, they must also be in equilibrium through the mediation of the solution.

Prob. 60. — Vapor-Pressure of a System Composed of Bromine and Water. — A system composed of bromine and water at 25° may consist of three phases; namely, a liquid solution of little bromine in much water (which may be called the water phase), a liquid solution of little water in much bromine (which may be called the bromine phase), and a gaseous phase containing the vapors of water and of bromine. *a.* Sketch a lettered diagram like Fig. 5 suitable for showing the conditions of equilibrium of this system. *b.* Show that perpetual motion could be realized unless certain (clearly specified) vapor-pressure conditions are satisfied.

IV. THE SECOND LAW OF THERMODYNAMICS
APPLIED TO PROCESSES AT DIFFERENT
TEMPERATURES.

26. General Statement of the Second Law of Thermodynamics. — A principle even broader than that of the impossibility of perpetual motion was long ago discovered (*Carnot, 1824*), a principle that is applicable not only to isothermal processes, but also to those taking place at different temperatures. To express this principle, now known as the *second law of thermodynamics*, in its general aspects various statements have been formulated; but probably the clearest of these is the following: *A process whose final result is only a transformation of heat into work is an impossibility (Planck, 1890).* For example, a process whose final results are only raising a weight and cooling a reservoir is impossible.

The perpetual-motion principle (*II, 16*) stating that work can not be produced from heat in surroundings at a single temperature when there is no permanent change in the state of the system employed for the transformation is evidently a logical consequence of this general statement of the second law of thermodynamics.

Prob. 61. — Production of Work from Heat at Constant Temperature. — When a gas that is placed in a reservoir of large heat-capacity and definite temperature expands against an external pressure, it produces work and withdraws from the reservoir a quantity of heat. State why this transformation of heat into work is not a contradiction of the second law of thermodynamics.

When different temperatures prevail in the surroundings, however, the second law does permit the production of work out of heat, even when the system undergoes no permanent change in state; for then another thing occurs in the surroundings, namely, the transfer of another quantity of heat from one temperature to another temperature. Thus when different temperatures prevail in the surroundings, a cyclical process (*II, 16*) can be carried out by which a quantity of heat is withdrawn from surroundings at a higher temperature, a fraction of this heat is converted into work, and the remainder of the heat is given out to surroundings at a lower temperature.

27. Derivation of the Fundamental Second-Law Equation. — To illustrate the character of cyclical processes by which heat may be transformed into work, and to determine the fraction of the heat which can be so transformed, consider the following four-step reversible process, known as the *Carnot cycle*, carried out with a system consisting of N mols of hydrogen gas, as shown in Fig. 6 by the diagram marked HYDROGEN PROCESS:

Start with the gas at a temperature T_1 and a volume v_1 contained in a cylinder closed with a weighted frictionless piston.

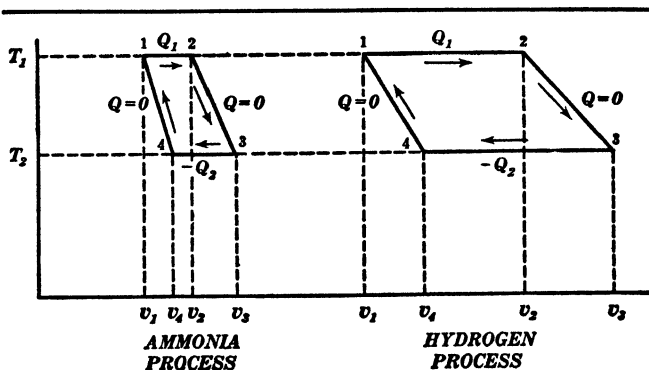
(1) Place the gas in a large heat-reservoir at T_1 , and expand it (isothermally) by a reversible process, so as to produce the maximum work, till it takes up from the reservoir at T_1 a certain quantity of heat Q_1 , whereby its volume becomes v_2 .

(2) Heat-insulate the gas (so that there can be no passage of heat to or from the surroundings), and expand it (adiabatically) by a reversible process till its volume becomes v_3 and its temperature falls to T_2 , which occurs because the gas loses energy equivalent to the work produced in the surroundings, since by the first-law equation $-\Delta E = W$ when $Q = 0$ (II, 2).

(3) Place the gas in a large heat-reservoir at T_2 , and compress the gas (isothermally) by a reversible process till it has such a volume that in step 4 it will be restored to its initial state. Hereby the gas gives to the reservoir at T_2 a quantity of heat $-Q_2$.

(4) Heat-insulate the gas from the surroundings, and compress it (adiabatically) by a reversible process till its temperature becomes T_1 and its volume v_1 .

FIGURE 6. DERIVATION OF CARNOT'S PRINCIPLE.



The net result of this reversible cyclical process is evidently as follows: a quantity of heat Q_i has been withdrawn from the surroundings at temperature T_i ; a portion $-Q_s^H$ of this heat has been transferred to the surroundings at temperature T_s ; and the remainder $Q_i + Q_s^H$ has been converted into work, in accordance with the first law of thermodynamics. Thus only a definite fraction, equal to $(Q_i + Q_s^H)/Q_i$, of the heat Q_i withdrawn from the surroundings at the (higher) temperature T_i has by this reversible cyclical process been transformed into work.

It will now be shown that the second law requires that the maximum work obtainable from a definite quantity of heat withdrawn from surroundings at one definite temperature and transferred in part to surroundings at another definite temperature is not dependent on the nature of the system nor on the reversible process employed for the transformation. For this purpose consider two reversible cyclical processes to be carried out with different systems under different conditions, and conceive that these processes convert into work unequal fractions of the heat taken up at the higher temperature. One of these processes is that just described (the HYDROGEN PROCESS of Fig. 6) carried out with a perfect gas at very small pressures; and the other process (the AMMONIA PROCESS of Fig. 6) consists of a corresponding series of operations at the same two temperatures T_i and T_s carried out with an imperfect gas at higher pressures. Consider that the isothermal expansion in the first step of each process is continued till the same quantity of heat Q_i is withdrawn from the heat-reservoir at T_i ; and imagine that of this heat Q_i taken up at T_i the fraction x_H converted into work by the hydrogen process is *greater* than the fraction x_A converted into work by the ammonia process. Consider now that the hydrogen process taking place as above described is followed by the ammonia process taking place in the direction opposite to that described. Evidently the net result of these combined processes would be nothing but the production in the surroundings of a quantity of work equal to $(x_H - x_A)Q_i$ and the withdrawal of an equivalent quantity of heat from the heat-reservoir at T_s ; but such a result is impossible according to the general statement of the second law of thermodynamics (II, 26). If the fraction x_H were *less* than the fraction x_A , a similar result would be attained

by causing the ammonia process to take place in the direction described and the hydrogen process to take place in the direction opposite to that described.

This important conclusion may be generalized by the following statement, known as *Carnot's principle*: A definite (maximum) quantity of work ΣW_R can be produced by a cyclical process when a definite quantity of heat Q_1 is taken up at any temperature T_1 and the heat not so transformed into work is transferred to a temperature T_2 ; and this quantity of work is not dependent on the nature of the system nor of the reversible process employed, but is determined solely by the two temperatures (*Carnot, 1824*). That is:

$$\Sigma W_R / Q_1 = f(T_1, T_2). \quad (48)$$

This principle greatly facilitates the determination of the relation between the temperatures and the fraction of heat transformable into work; for evidently it is now only necessary to determine what that relation is for a single reversible cyclical process. For this purpose it is natural to employ a process with a system consisting of a perfect gas, since its energy relations are definitely known and temperature has been defined with reference to its pressure-volume product (*I, 11, 14*). In fact, the relation was first derived by a reversible cyclical process like that shown in Fig. 6 carried out with a perfect gas. Here will be considered, however, a different type of perfect-gas process — one for which the work can be more simply evaluated and one which is further simplified by operating between two temperatures differing only by an infinitesimal amount.

Prob. 62. — Derivation of the Second-Law Equation. —

Consider the following cyclical process carried out reversibly with N mols of a perfect gas contained in a cylinder closed with a weighted frictionless piston:

Start with the gas at temperature T and volume v_1 .

(1) Keeping the gas in a large heat-reservoir at T , diminish gradually the weight on the piston and cause the gas to expand till its volume becomes v_2 .

(2) Fix the piston so that the volume must remain constant, and place the gas in a large heat-reservoir at $T + dT$.

(3) Keeping the gas in the heat-reservoir at the temperature $T + dT$, compress it by releasing the piston and gradually increas-

ing the weight upon it till the volume of the gas has been restored to its original value v_1 .

(4) Fix the piston again so as to keep the volume constant, and place the gas in a heat-reservoir at the temperature T .

a. Represent this process by a lettered diagram similar to those in Fig. 6. *b.* Formulate expressions for the quantities of work and heat (see II, 9) involved in the separate steps of this process, and tabulate them under the headings, work produced, heat withdrawn at T , heat withdrawn at $T + dT$. At the foot of the table formulate a corresponding expression for the sum of each of these three quantities so as to represent the net result of the whole process. *c.* Formulate a relation between the work ΣW_R produced by the whole process and the heat Q withdrawn from the surroundings at T ; noting that the heat-effect in step 4 is infinitesimal.

Since it was previously shown in deriving Carnot's principle (Eq. 48) that the second law requires that the same quantity of work be produced when a definite quantity of heat is transferred from one definite temperature to another by any reversible cyclical process whatever, it is evident that the equation just derived for one such process is an exact expression of the second law for every such process. This equation therefore expresses one of the fundamental characteristics of energy itself.

The equation just obtained, which will be called simply the *second-law equation*, may be written in the form:

$$\Sigma W_R / Q_R = - dT / T. \quad (49)$$

In this equation ΣW_R denotes the algebraic sum of all the quantities of work produced in any reversible cyclical process taking place at two temperatures T and $T + dT$ in which the quantity of heat Q_R is withdrawn from the surroundings at the temperature T . The work-quantity ΣW_R is obviously infinitesimal in correspondence with the infinitesimal temperature-difference dT .

Prob. 63. — Corollaries from the Second-Law Equation. —

Show that the second-law equation leads to the following conclusions: *a.* When there is no difference of temperature in the surroundings heat can not be transformed at all into work by any cyclical process. *b.* In order to carry heat from a lower to a higher temperature work must be withdrawn from the surroundings. *c.* The fraction of the heat transformable into work for a given difference in temperature is greater, the lower the temperatures. *d.* By a reversible process operating at dT° and 0°A , the heat absorbed at dT° would be completely converted into work.

28. Work Producing from Heat in Surroundings at Two Finitely Different Temperatures. — When a quantity of heat Q_1 is taken up at T_1 , and the quantity of it — Q_2 not transformed into work is transferred to a finitely different temperature T_2 , with no heat-interchange between the system and surroundings at intermediate temperatures, it can be shown that the second law leads to the following relations (of which the last follows from the first, since $\Sigma W_s = Q_1 + Q_2$):

$$\frac{\Sigma W_s}{Q_1} = \frac{T_1 - T_2}{T_1}; \quad \text{or} \quad \frac{Q_1}{-Q_2} = \frac{T_1}{T_2}. \quad (50)$$

The following derivations and considerations may be omitted since the infinitesimal form of the second-law equation (Eq. 49) is always employed in physicochemical applications. These considerations are presented here mainly because they afford a fuller appreciation of general thermodynamics. Moreover, the finite equation (Eq. 50) is of importance, since it leads to a clear definition of the so-called thermodynamic temperature-scale, and since it is much used in engineering applications. Furthermore, its usual derivation by consideration of the Carnot cycle (Prob. 66) involves important energy relations (Prob. 64); and the special derivation here presented (Prob. 65) is of interest because of its simplicity and because it brings out the conditions that must be fulfilled in order that a process involving differences of temperature may be reversible.

**** Conditions of Reversibility of Processes
Involving Different Temperatures.**

The above-given finite form of the second-law equation was originally derived (as in Prob. 66) by finding expressions for the quantities of work and heat involved in a Carnot cycle carried out with a perfect gas. The equation can be much more simply obtained (*Mach, 1896*) by considering a reversible cyclical process similar to that already used (Prob. 62) for deriving the infinitesimal form of the second-law equation; namely, by considering a process (as in Prob. 65) which involves cooling the expanded gas at the constant volume v_2 from temperature T_1 to temperature T_2 , and heating the compressed gas at the constant volume v_1 from temperature T_2 to temperature T_1 . A procedure must, however, be devised for making these processes of cooling and heating reversible. For, if the gas at volume v_2 were cooled from T_1 to T_2 by placing it directly in the heat-reservoir at T_2 , and if the gas at volume v_1 were heated from T_2 to T_1 by placing it directly in the heat-reservoir at T_1 , it is evident that a finite quantity of heat (equal to $N \bar{C}_v (T_1 - T_2)$ if $\bar{C}_v$ be constant) would be transferred

from the higher temperature T_1 to the lower temperature T_2 , without producing the work which heat so passing is always capable of producing. This transfer of heat and attendant loss of work can, however, be avoided by cooling the gas from T_1 to T_2 with the aid of an infinite series of heat-reservoirs whose temperatures vary progressively from T_1 to T_2 by infinitesimal amounts dT , and by using these same reservoirs for heating the gas from T_2 to T_1 . In this way the heat stored in the series of reservoirs in the cooling process flows out of them back into the system in the heating process at a temperature which is always less by only an infinitesimal amount.

These considerations constitute an extension of the conditions that determine whether a process be directly reversible, of which the primary criterion (II, 17), it may be recalled, is whether the process can be carried out in the opposite direction without producing any resultant change in the system or in the surroundings. Namely, the above considerations show that to make a process directly reversible and cause it to produce the maximum work—just as in a volume change the applied pressure must be kept substantially equal to that of the system, and just as in a voltaic change the applied electromotive force must be kept substantially equal to that of the cell—so in the case of a flow of heat between the system and the surroundings the temperature of the heat-reservoir must be substantially equal to that of the system.

In view of these facts, a *general condition of reversibility* may be stated as follows: In order that a change may take place reversibly, the property of the system whose magnitude determines whether the change occurs must be balanced in the surroundings by an opposing agency of the same kind whose magnitude is equal within an infinitesimal amount.

**** Reversible Adiabatic Expansion of a Perfect Gas.**

Since an adiabatic process is by definition (II, 5) a process in which the system exchanges no heat with the surroundings (so that $dQ = 0$), it follows from the first-law equation $dE = dQ - dW$ that for a reversible adiabatic expansion of any system at the pressure p , attended by changes dv and dT in volume and temperature, the energy-content increase $dE = -p dv$. Since the energy-content of a system in the perfect-gas state is determined solely by its temperature (II, 9), it follows further that $dE = C_v dT$. Hence, for the reversible adiabatic expansion of a system in the perfect-gas state:

$$C_v dT = -p dv. \quad (51)$$

From this expression, with the aid of the perfect-gas equation, there can be derived by substitution and integration expres-

sions for the corresponding finite changes in pressure and volume and in volume and temperature that attend the adiabatic expansion of a perfect gas whose molar heat-capacity at constant volume $\tilde{C}_v$ is independent of its temperature (as well as of its volume at constant temperature). These expressions are as follows:

$$p v^{(C_p/C_v)} = \text{const.} \quad (52). \quad T v^{(R/\tilde{C}_v)} = \text{const.} \quad (53)$$

Prob. 64. — Derivation of Expressions for the Adiabatic Expansion of a Perfect Gas. — Derive the equations just given.

**** Derivation of the Second-Law Equation in Its Finite Form.**

Prob. 65. — Derivation by a Cyclical Process Involving Cooling and Heating at Constant Volume. — a. Formulate the quantity of work produced in each step and the quantity of heat withdrawn at T_1 by the following reversible cyclical process:

- (1) Expand isothermally N mols of a perfect gas at T_1 from v_1 to v_2 .
- (2) Cool the gas from T_1 to T_2 at the constant volume v_2 .
- (3) Compress isothermally the gas at T_2 from v_2 to v_1 .
- (4) Heat the gas from T_2 to T_1 at the constant volume v_1 .

b. From the formulated expressions derive Eq. 50. *c.* Show whether, in order that this derivation may be valid, the heat-capacity of the gas must be independent of its volume, and whether it must be independent of its temperature; and state whether a perfect gas satisfies each of these conditions.

Prob. 66. — Derivation by a Carnot Cyclical Process Involving Changing the Temperature by Adiabatic Expansion and Compression. — a. Formulate and tabulate expressions for the work produced W_R , the heat absorbed Q , and energy-content increase $E_2 - E_1$ in each step of the hydrogen process shown in Fig. 6 and described in the text preceding that figure (II, 27); assuming the hydrogen to be in the perfect-gas state, so that its p - v - T relations may be expressed by $p v = N R T$, and so that its energy-content and heat-capacity at any definite temperature may be independent of its volume (II, 9). Express these quantities in terms of volumes and temperatures for steps 1 and 3, and in terms of the heat-capacity $(C_v)_2$ or $(C_v)_4$ and of the temperatures for steps 2 and 4. *b.* Show from the energy-content law of perfect gases (II, 9) that the work produced has equal and opposite values in steps 2 and 4; and formulate an expression for the total work ΣW_R produced by the whole cyclical process. *c.* Formulate a differential equation expressing a first-law relation between the volume-increase dv and the temperature-decrease $-dT$ attending any adiabatic expansion. In this equation replace the pressure p with the aid of the perfect-gas equation, and formulate the definite integrals that result from applying the equation to steps 2 and 4

of the process. From these integrals derive, with the aid of the energy-content law for perfect gases, the finite second-law equation (Eq. 50).

**** Thermodynamic Scale of Absolute Temperature.**

Upon the second law of thermodynamics may be based a scale of temperature which is truly absolute in the sense that it depends, not on the effect of temperature on any physical property of any substance or type of substance, but on the characteristics of energy itself. For, in virtue of the Carnot principle $Q_1/-Q_2 = f(T_1, T_2)$, it is evidently possible to assume, as is in fact done in defining *thermodynamic temperatures* (Kelvin, 1848), that any two temperatures are directly proportional to the quantities of heat withdrawn from or imparted to the surroundings in a reversible cyclical process operating at those two temperatures; in other words, it can be and is assumed that the function defining thermodynamic temperature has the form $T_1/T_2 = Q_1/-Q_2$. It has, however, been shown (by Eq. 50) that the second law has this very form when absolute temperature has been defined to be proportional to the pressure-volume product of a perfect gas; thus proving that absolute temperature has identical values whether it is defined thermodynamically or by the perfect-gas equation.

**** 29. The Entropy Concept and Its Use in Expressing the Laws of Thermodynamics.** — It has already been shown (Probs. 65, 66; II, 28) that the equation $Q_1/(-Q_2) = T_1/T_2$ (Eq. 50; II, 28) formulates the relation between the quantities of heat Q_1 and $-Q_2$ absorbed at T_1 and given off at T_2 , respectively, in any two-temperature reversible cyclical process (like a Carnot process with a perfect gas) in which there is no resultant heat effect at the intermediate temperatures. This equation may also be written in the forms:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0; \quad \text{and} \quad \frac{Q_1}{T_1} = -\frac{Q_2}{T_2}. \quad (54)$$

The first equation expresses the principle that when a system returns to its initial state after undergoing a two-temperature reversible cyclical process, the sum of the quantities Q/T involved is zero. The second equation expresses the principle that when a system changes from a specified state at T_1 to a specified state at T_2 , the value Q_1/T_1 of the quantity Q/T by one reversible

** Even in longer courses, Arts. 29, 30, 32 (but not 31) may be postponed until there is occasion to use the principles involved.

process is equal to its value $-Q_s/T_s$ by another reversible process. The last would be true, for example, if one mol of a perfect gas changed from a volume $\tilde{v}_1$ at T_1 to volume v_s at T_s by the two different processes involved in a Carnot cycle (Fig. 6; II, 27); namely, (1) by isothermal expansion from volume $\tilde{v}_1$ to volume $\tilde{v}_s$ at T_1 with an adsorption of heat Q_1 , followed by adiabatic expansion to volume v_s between T_1 and T_s , and (2) by adiabatic expansion from volume $\tilde{v}_1$ to volume v_i between T_1 and T_s , followed by isothermal expansion to volume $\tilde{v}_s$ at T_s with adsorption of heat Q_s ; that is to say, Q_1/T_1 would equal Q_s/T_s .

The quantity Q/T in any reversible process is therefore one whose value is determined solely by the change in state of the system, which in this case may involve change in its temperature. Hence the quantity Q_R/T measures a function, called the *entropy-content* or simply the *entropy* S of the system (Clausius, 1854) whose change, $S_s - S_i$, is determined solely by the initial state (St_i) and the final state (St_s). That is,

$$S_s - S_i = f(St_s, St_i). \quad (55)$$

Since any change in state from T_1 to T_s can be brought about by the combination of a series of successive isothermal and adiabatic processes (like those in either half of a Carnot cycle) each involving, if need be, infinitesimal changes dT in temperature, the general expressions for the change in entropy of a system are:

$$dS = \frac{dQ_R}{T}; \quad \text{and} \quad S_s - S_i = \int_1^s \frac{dQ_R}{T}. \quad (56)$$

That is to say, the increase in the entropy of a system in changing from one state to another is by definition equal to the integral of all the quantities of heat absorbed, each divided by the corresponding absolute temperature when the system passes from one state to the other state by a reversible process or by a series of such processes.

Changes in entropy may be evaluated in various units corresponding to the energy-unit in which the heat is expressed. As the calorie is commonly employed in this book and in most publications, the usual entropy-unit is the cal./centigrade-degree.

In view of the foregoing considerations the second law of thermodynamics is expressed in terms of the entropy concept by Eqs. 55 and 56.

It will be seen that entropy S is, like energy-content E , heat-content H , work-content A , or free-energy F , a thermodynamic function characterizing the state of systems. Like the equations for E and H (Table I; II, 6), the entropy relations are applicable to changes in state involving different temperatures. The concept of work-content previously considered was based on the impossibility of perpetual motion of the second kind, and consequently the general expressions for evaluating changes in A and F (Table III; II, 22) derived from this principle are limited to isothermal changes. This limitation in regard to the concept of work-content and free-energy is removed in general thermodynamics by defining these functions in terms of entropy and energy-content or heat-content (*Helmholtz, 1882*) by the following equations applicable at any temperature:

$$A = E - TS; \quad \text{and} \quad F = H - TS. \quad (57)$$

This definition serves to correlate more completely the system of thermodynamic functions. The relation $F = A + pv$, defining the free-energy of a system in terms of its work-content and pressure-volume product (Eq. 38; II, 22), evidently follows from Eq. 57 and the relation $H = E + pv$, defining heat-content (Eq. 17; II, 6).

The relations between the entropy-change and the other thermodynamic functions are given for changes in state at constant temperature by the important equations:

$$TdS = dH - dF = dE - dA;$$

and

$$T\Delta S = \Delta H - \Delta F = \Delta E - \Delta A. \quad \text{ce i)}$$

These relations follow directly from Eq. 57. They may also be derived from the fundamental definition $dS = dQ_a/T$ and from the relations between the other thermodynamic functions and work and heat quantities (Table I; II, 6; Table III; II, 22).

It is evident that a knowledge of the changes in entropy-content and heat-content attending an isothermal change in state of a system makes it possible to calculate by these equations its decrease in free-energy, and therefore its equilibrium conditions

(II, 23) — facts which indicate the great chemical significance of these equations.

Prob. 67. — Relations between Changes in Entropy and Changes in Other Thermodynamic Functions. — Derive Eq. 58 from the definition of entropy and the previously formulated relations concerning other thermodynamic quantities (see Tables I and III; II, 6, 22).

Prob. 68. — Changes in Work-Content and in Free Energy Attending Isothermal Changes. — Derive the equations formulated in Table III (II, 22) from the general definitions of heat-content by Eq. 17 (II, 6), and of work-content and free energy by Eq. 57, the first law equation, and the entropy concept.

Prob. 69. — Change in Work-Content of a System Heated at Constant Volume, and in Free Energy Heated at Constant Pressure. — Derive partial-derivative expressions for the changes named in the title, namely for $(\partial A/\partial T)_v$ and for $(\partial F/\partial T)_p$ with the aid of Eq. 57, the first law equation, and the entropy concept.
Ans. $(-\partial A/\partial T)_v = (-\partial F/\partial T)_p = S$.

Prob. 70. — Entropy-Increase of a Chemical Reaction Calculated from its Change in Heat-Content and in Free Energy. — The reaction $\text{H}_2(\text{g}) + \text{HgO}(\text{s}) = \text{Hg}(\text{l}) + \text{H}_2\text{O}(\text{l})$ at 25° and 1 atm. is attended by a heat-content decrease of 46,770 cal.; and when taking place in the voltaic cell, $\text{H}_2(1 \text{ atm.}), \text{KOH}(0.1 \text{ f.}), \text{HgO}(\text{s}) + \text{Hg}(\text{l})$, it produces an electromotive force of 0.9265 volt. Calculate the entropy-increase attending this reaction at 25° .

**** 30. Changes in Entropy-Content Attending Changes in the Physical States of Substances.** — Table V contains expressions for the entropy-increase attending various typical physical changes. These expressions were derived (Eq. 56) by

TABLE V. ENTROPY-INCREASE ATTENDING PHYSICAL CHANGES OF ONE MOL OR ONE FORMULAR WEIGHT OF SUBSTANCE.

<i>Initial State</i>	<i>Final State</i>	<i>Entropy-Increase</i>
Perfect gas at p_1, T	Perfect gas at p_2, T	$R \ln (p_1/p_2)$
Liquid at p, T	Saturated vapor at p, T	$\Delta \tilde{H}_v/T$
Substance at p, T	Substance at $p, T + dT$	$\tilde{C}_p dT/T$
Substance at $\tilde{v}, T$	Substance at $\tilde{v}, T + dT$	$\tilde{C}_v dT/T$
Substance at $p_1, \tilde{v}_1, T_1$	Substance at $p_2, \tilde{v}_2, T_2$ (such that $Q_R = 0$)	Zero

dividing by the temperature T the heat-effect (dQ_a) attending the change in state when it takes place reversibly (with production of the maximum work), and integrating when the change is finite.

Prob. 71. — Entropy-Increase Attending the Isothermal Expansion of a Perfect Gas. — State the reasoning involved in deriving the entropy-increase attending the isothermal expansion of a perfect gas.

Prob. 72. — Entropy-Changes Attending Changes in Aggregation State and Temperature. — Calculate the difference in the entropies (in cal./degree) of 1 fwt. of ice at 0° and 1 atm. and of 1 fwt. of steam at 100° and 1 atm. from the heats of fusion and vaporization (79.7 and 540 cal. per gram) and from the heat-capacity of water, assuming this to be constant between 0° and 100° at its mean value (*I*, 11).

Prob. 73. — Entropy-Change Attending the Heating of a Gas of Variable Heat-Capacity. — Calculate from the data of Prob. 6 (*II*, 4) the increase in the molar entropy of nitrogen when it is heated from 20° to 600°C .

31. Effect of Temperature on the Pressure at which Phases Are in Equilibrium. Clapeyron's Equation. — From the second-law equation may be derived the effect of temperature on the pressure, or conversely the effect of pressure on the temperature, at which different phases of a pure substance coexist in equilibrium with one another (*I*, 18). For example, there may be derived the effect of temperature on the vapor-pressure of a liquid or solid, or the effect of pressure on the melting-point of a solid or on the transition-temperature of two crystalline forms.

An expression for the effect of temperature on vapor-pressure (*Clapeyron*, 1834) may be derived with the aid of the following reversible cyclical process, illustrated by Fig. 7.

Start with some definite quantity of any pure substance in the state of liquid (or solid) at a temperature T and at a pressure p equal to its vapor-pressure, which is the pressure at which the liquid and vapor are in equilibrium.

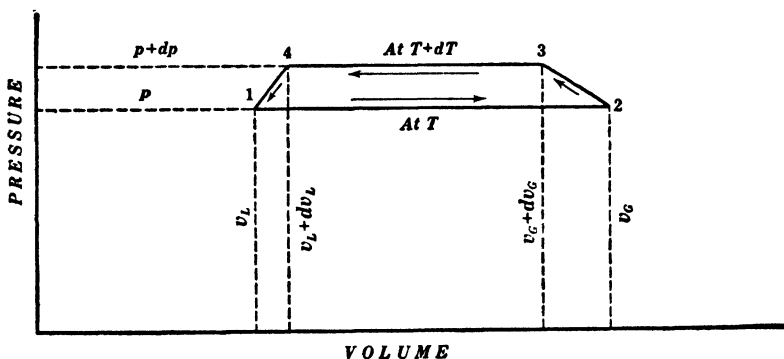
(1) Vaporize the liquid at this pressure and temperature.

(2) Heat the vapor to $T + dT$, and change its pressure to $p + dp$, this being at $T + dT$ the pressure of the saturated vapor, equal to the vapor-pressure of the liquid.

(3) Condense the vapor to liquid at this (constant) temperature and pressure.

(4) Cool the liquid to T , and change its pressure to p , thereby completing the cycle.

FIGURE 7. DERIVATION OF CLAPEYRON EQUATION.



The volume-changes attending these four steps are shown in Fig. 7; and the corresponding quantities of work, obtained by multiplying each of these by the prevailing pressure, are:

$$\begin{array}{ll} (1) \quad p(v_G - v_L); & (2) \quad p \, dv_G; \\ (3) \quad -(p + dp)(v_G + dv_G - v_L - dv_L); & (4) \quad -p \, dv_L. \end{array}$$

The total work ΣW_R produced by the whole cyclical process is the sum of these four quantities; and this sum, except for infinitesimals of the second order, is equal to $-dp(v_G - v_L)$. The heat Q_R absorbed by the system at T is evidently the heat of vaporization of the quantity of liquid taken. Substitution of these values in the second-law equation (Eq. 49) gives:

$$-dp(v_G - v_L) = -\frac{Q_R}{T} dT. \quad (59)$$

Noting that $v_G - v_L$ is the increase in volume Δv , and that Q_R is equal to the increase in heat-content ΔH , attending the vaporization of any specified quantity of substance at temperature T under the equilibrium pressure p , the above equation may be written in terms of properties characteristic of the substance in

the following form, known as the *Clapeyron equation*:

$$\frac{dp}{dT} = \frac{1}{T} \frac{\Delta H}{\Delta v}. \quad (60)$$

This equation evidently expresses the rate of change with the temperature of the vapor-pressure of any pure liquid or solid substance at temperature T .

Prob. 74. — Effect of Temperature on Vapor-Pressure. —

a. Calculate the change of vapor-pressure of water at 100° in millimeters per degree from the following data: at 100° and 1 atm. the heat of vaporization of H_2O is 9720 cal.; the specific volume of liquid water is 1.043 ml., and that of water-vapor is 1677 ml. Note that the heat quantity ΔH and the work quantity $dp \cdot \Delta v$ must be expressed in the same energy units, for example in ergs, in which case the pressure will be in dynes per sqcm. *b.* Find the percentage error in dp/dT that would be made by neglecting the volume of the liquid. *c.* State the percentage error in dp/dT that would be made by assuming that the saturated vapor is a perfect gas (see Prob. 1c; II, 3).

The Clapeyron equation can be simplified by making the assumptions that the volume of the liquid or solid is negligible in comparison with that of the saturated vapor, and that the vapor conforms to the perfect-gas laws. The *approximate Clapeyron equation* so obtained is:

$$\frac{d \ln p}{dT} = \frac{\Delta \tilde{H}}{RT^2}. \quad (61)$$

In this equation p denotes the vapor-pressure of the liquid or solid substance at the temperature T , and $\Delta \tilde{H}$ is equal to its molar heat of vaporization (II, 7) at that temperature.

The approximate equation has the advantage that it can be directly integrated between two temperatures, provided the assumption be made that the heat of vaporization is constant between them — an assumption that is usually attended by small error when the temperature-interval is small. The resulting expression is:

$$\ln \frac{p_2}{p_1} = \frac{\Delta \tilde{H}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \quad (62)$$

Prob. 75. — Derivation and Integration of the Approximate Clapeyron Equation. — a. Derive Eq. 61 by neglecting the volume of the liquid in comparison with that of the saturated vapor, and

by assuming the vapor to be a perfect gas. *b.* Derive Eq. 62, assuming that $\Delta\tilde{H}$ does not vary with the temperature.

Prob. 76. — Vapor-Pressure Evaluated by the Approximate Clapeyron Equation. — a. Calculate the vapor-pressure of water at 75° from that at 100° and from its molar heat of vaporization (9720 cal.) at 100° . *b.* Find the percentage deviation of this calculated value from the actual vapor-pressure (289.1 mm.); and state the three approximate assumptions involved which must account for this deviation. *Ans. a,* 296 mm.

Note. — By using the heat of vaporization (9860 cal.) at the mean temperature 87.5° , the calculated vapor-pressure is found to be 292.5 mm., in closer agreement with the observed value, since the error due to variation of the heat of vaporization is thereby almost wholly eliminated.

The exact Clapeyron equation (Eq. 60) is applicable to phase transformations other than vaporization. For its derivation shows that the same form of expression would be obtained in the case of any reversible cyclical process whose first and third steps consist in any change in phase which takes place at constant temperatures T and $T + dT$ under the constant pressures p and $p + dp$ at which the two phases are in equilibrium. The equation therefore applies to the fusion of ice or other solids, in which case dT/dp denotes the rate of change in its melting-point T with the applied pressure, Δv denotes the increase in volume attending the fusion of any specified quantity of the solid, and ΔH the increase in heat-content attending the fusion of this same quantity of solid. The equation also expresses the effect of pressure on the transition-temperature of one solid phase into another; for example, of rhombic sulfur into monoclinic sulfur.

Prob. 77. — Effect of Pressure on Melting-Point. — a. Calculate the variation per atmosphere of the melting-point of ice from the facts that at 0° and 1 atm. the densities of ice and water are 0.9168 and 0.9999, respectively, and that the heat of fusion of ice is 79.7 cal. per gram. *b.* Find the freezing-point of pure (air-free) water at 1 atm. from this result and from the conditions at the triple-point (*I, 18*). Explain why this value is not zero centigrade (*I, 11*). *Ans. a,* -0.0075° . *b,* 0.0023° .

Similar considerations show that the Clapeyron equation is applicable not only to any one-component system of two phases but to any other univariant system. It applies, for example, to the two-component system made up of the three phases, $\text{Ag}_2\text{O}(s)$,

Ag(s) , and $\text{O}_2(\text{g})$. For this case the temperature-coefficient dp/dT of the dissociation pressure of silver oxide at any temperature T can be calculated by substituting in the Clapeyron equation for ΔH the increase in heat-content, and for Δv the increase in volume which attends the dissociation of any definite quantity of silver oxide under equilibrium conditions at the temperature T .

**** Prob. 78. — Derivation of the Clapeyron Equation Through the Entropy Concept.** — The system consisting of the three phases $\text{Ag}_2\text{O(s)}$, Ag(s) , and $\text{O}_2(\text{g})$ is in equilibrium at the temperature T and the pressure p and also at the temperature $T + dT$ and the pressure $p + dp$. Consider for definiteness the change in state $2 \text{Ag}_2\text{O(s)} = 4 \text{Ag(s)} + \text{O}_2(\text{g})$ in one case at T and p , and in another case at $T + dT$ and $p + dp$. Let the volumes, free energies, and entropies of the system in its initial state (in the state of $\text{Ag}_2\text{O(s)}$) be v_1 , F_1 , S_1 at T and p , and $v_1 + dv_1$, $F_1 + dF_1$, $S_1 + dS_1$ at $T + dT$ and $p + dp$; and the volumes, free energies, and entropies in its final state (in the state of Ag(s) and $\text{O}_2(\text{g})$) be v_2 , F_2 , S_2 at T and p , and $v_2 + dv_2$, $F_2 + dF_2$, $S_2 + dS_2$ at $T + dT$ and $p + dp$. The increase in free energy attending the change in state will then be $F_2 - F_1 = \Delta F$ at T and p , and $(F_2 + dF_2) - (F_1 + dF_1) = \Delta F + d\Delta F$ at $T + dT$ and $p + dp$.
a. From the criteria of equilibrium conditions within any isothermal system considered in *II*, 23, show that $dF_2 - dF_1 = d\Delta F = 0$.
b. With the aid of the general equation $F = H - TS$, the first law equation, and the entropy concept derive expressions for dF_1 in terms of v_1 , S_1 , dT and dp , and for dF_2 in terms of v_2 , S_2 , dT and dp , noting that in general $dF = (\partial F/\partial T)_p dT + (\partial F/\partial p)_T dp$.
c. By equating these expressions derive the Clapeyron equation.

Prob. 79. — Heat of Dissociation from the Effect of Temperature on Dissociation Pressure. — The dissociation pressure of silver oxide is 422 mm. at 173° , and 605 mm. at 183° . Calculate the heat of dissociation (under equilibrium conditions) of $1 \text{Ag}_2\text{O}$, assuming this heat-effect to be independent of temperature, and that the volume increase on dissociation is equal to the volume of the oxygen produced. (The value found at 18° from calorimetric measurements is 6950 cal.)

Prob. 80. — Application of the Clapeyron Equation to Solutions. — A solution of any nonvolatile solute in a given solvent can be made in effect univariant by specifying a definite composition of the solution. In applying the Clapeyron equation to determine the effect of temperature on the vapor-pressure of a 10% NaCl solution, specify the change in state to which the quantities ΔH and Δv would correspond.

32. The Effect of Temperature on the Free Energy Decrease Attending Any Isothermal Change in State. — By applying the fundamental second-law equation to certain reversible cyclical processes there can be derived, as shown in Probs. 81 and 82, the differential equations displayed below which express the change with the temperature of the decreases $-\Delta A$ and $-\Delta F$ in the work-content and in the free energy of a system attending any isothermal change in its state. This derivation is based on the concept of work-content and the definition of free energy (Eqs. 37, 38; II, 22) formed from a consideration of reversible processes taking place at a single temperature. These differential equations may also be derived, as shown in ** Prob. 83, from the entropy concept and the more general definitions of work-content and of free energy (Eq. 57; II, 29) in terms of entropy, temperature, and energy-content or heat-content.

$$\left(\frac{d(-\Delta A)}{dT} \right)_v = \frac{\Delta E - \Delta A}{T} = \Delta S, \quad (63)$$

$$\left(\frac{d(-\Delta F)}{dT} \right)_p = \frac{\Delta H - \Delta F}{T} = \Delta S. \quad (64)$$

These equations are general expressions of the second-law in forms especially convenient in considerations relating to chemical equilibrium and electromotive force. It is important fully to appreciate the significance of the quantities occurring in them and the case to which each equation is applicable. These are shown by the derivations of the equations to be as follows. The quantities $-\Delta A$ and $-\Delta F$ denote the decreases in the work-content and in the free energy of the system which attend any isothermal change in its state at the temperature T ; and ΔE , ΔH and ΔS denote the accompanying increases in its energy-content, heat-content, and entropy. The differential quantities $d(-\Delta A)$ and $d(-\Delta F)$ signify that when the same change in state takes place at $T + dT$, instead of at T , it is attended by a work-content decrease of $-\Delta A + d(-\Delta A)$ and by a free energy decrease of $-\Delta F + d(-\Delta F)$, instead of one of $-\Delta A$ and of $-\Delta F$. The subscript v in the work-content equation indicates, as shown in its derivation, that the equation is applicable to cases in which the initial volume v_1 , and also the final volume v_2 , of the system

is the same at T and at $T + dT$. Similarly, the subscript p indicates that the free energy equation is limited in its application to cases in which the initial pressure p_i , and also the final pressure p_s , of the system is the same at the two temperatures.

Derivation of the Work-Content and Free-Energy Equations.

Prob. 81. — To derive Eq. 63 consider a reversible cyclical process involving the following steps:

- (1) Any change in state of any system at the temperature T , by which a quantity of work W_R is produced;
- (2) a change in the temperature of the system at constant volume v_2 from T to $T + dT$;
- (3) a change in the state of the system at the temperature $T + dT$ which is the reverse of the change in state in the first step, this change being attended by a production of a quantity of work equal to $-(W_R + dW_R)$;
- (4) a change in the temperature of the system at constant volume v_1 from $T + dT$ to T .

a. Represent this process by a lettered diagram in which the ordinates denote temperatures and the abscissas volumes. *b.* Find an expression for ΣW_R for this process. *c.* By substituting it in the second-law equation and by making other appropriate substitutions, show that Eq. 63 results.

Prob. 82. — To derive Eq. 64, consider a reversible cyclical process just like that described in the preceding problem, except that in steps (2) and (4) the system is kept at constant pressure, instead of at constant volume. *a.* Represent this process by a lettered diagram in which the ordinates denote temperatures and the abscissas volumes, designating the pressures and volumes of the system at the beginning of each of the four steps by (1) p_i and v_i ; (2) p_s and v_s ; (3) p_s and $v_s + dv_s$; (4) p_i and $v_i + dv_i$. *b.* Find an expression for ΣW_R for this process. *c.* By substituting this expression in the second-law equation and making other appropriate substitutions based on the definition of heat-content by Eq. 17 (II, 6) and of $-\Delta F$ by Eq. 39 (II, 22), show that Eq. 64 results.

**** Prob. 83.** — *a.* Consider a definite system to undergo at any definite temperature T a definite change in state, for which $\Delta E = E_s - E_i$, $\Delta H = H_s - H_i$, $\Delta A = A_s - A_i$, $\Delta F = F_s - F_i$, $\Delta v = v_s - v_i$, and $\Delta p = p_s - p_i$. Derive from Eqs. 56 and 57 (II, 29) an expression (1) for $(\partial A_i / \partial T)_{v_i}$ and for $(\partial A_s / \partial T)_{v_s}$; and (2) for $(\partial F_i / \partial T)_{p_i}$ and for $(\partial F_s / \partial T)_{p_s}$. *b.* Let the same change in state considered in *a* take place at $T + dT$ with the under-

standing that the initial and final volumes v_i and v_g of the system are the same at $T + dT$ as at T . Noting that $(d\Delta A/dT)_p = (\partial A_g/\partial T)_{v_g} - (\partial A_i/\partial T)_{v_i}$, derive Eq. 63. *c.* By a similar procedure, derive Eq. 64. In this case let the change in state considered in *a* take place at $T + dT$ with the understanding that p_i and p_g are the same at the two temperatures.

In accordance with the practice adopted throughout this book, only the free energy equation (with omission of the subscript p) will hereafter be employed. For purposes of integration this equation is more conveniently written in the following forms:

$$d\left(\frac{-\Delta F}{T}\right) = \frac{\Delta H}{T^2} dT. \quad (65)$$

$$\frac{-\Delta F}{T} = \int \frac{\Delta H}{T^2} dT + I. \quad (66)$$

In applications of Eq. 66, the constant of integration I can obviously be eliminated by integrating between any definite temperature limits, T_1 and T_2 . This equation in any of its forms will be called the *second-law free energy* equation.

Prob. 84. — Proof of Identity of the Different Forms of the Free Energy Equation. — Show that the free energy equations 64 and 65 are identical by carrying out in the first member of Eq. 65 the indicated differentiation, and by making simple transformations.

Application of this fundamental equation to determine the effect of temperature on chemical equilibrium and on electromotive force will be fully considered in later chapters. It may, however, be here noted that, in the integration of the second term of Eq. 66, the given value of the heat-content increase may often be regarded as constant; but in the exact treatment it must be expressed as a function of the temperature.



PART II.

MOLECULAR AND IONIC THEORIES AND THE RELATED PROPERTIES OF SUBSTANCES IN VARIOUS AGGREGATION-STATES

CHAPTER III

THE PROPERTIES OF GASES AND THE MOLECULAR AND KINETIC THEORIES

I. AVOGADRO'S LAW AND DALTON'S LAW. MOLECULAR AND ATOMIC WEIGHTS. MOLECULAR STATE OF SUBSTANCES IN GASEOUS MIXTURES.

1. **Avogadro's Law.** — The laws determining the pressure-volume-temperature relations of any gas as its pressure approaches zero are expressed, as already shown (*I, 14*), by the *perfect-gas equation*

$$p v = N R T. \quad (1)$$

In this equation, the gas-constant R represents the value of $p v/T$ for one mol of any gas, and N denotes the number of mols of gas present (equal to m/M , where m is the mass and M the molar weight of the gas). It is often convenient to express these laws in terms of the gas density $\bar{m}$ (equal to m/v) or of the molal concentration c (equal to N/v), namely, as follows:

$$p = \bar{m} R T / M \quad (2); \quad p = c R T. \quad (3)$$

One mol or *one molar weight* has previously been empirically defined to be that weight of the gas which has the same value of $p v/T$ as 32 grams of oxygen when both are in the state of a perfect gas. The concept of mol, which is one of great chemical importance, will now be interpreted with respect to its molecular significance.

Besides the laws expressing the uniform physical behavior of gases, there was early discovered (*Gay-Lussac, 1808*) an important law as to the volumes of gases that enter into chemical reactions with one another. This law, known as the *law of combining volumes*, states that the quantities of the different substances that are involved in any definite chemical reaction have, when in the state of perfect gases, volumes at the same temperature and pressure, or expressed more generally values of $p v/T$, which are equal to one another or stand to one another in ratios of small whole numbers. This law, like other volume

laws of gases, is approximately true at a pressure of one atmosphere, and becomes exact as the pressure approaches zero. For example, the quantities of hydrogen and oxygen which unite to form water have volumes whose ratio is 2.0031 at 0° and 1 atm., but approaches exactly 2 as the pressure of the gases approaches zero; and the quantities of oxygen taken and water produced when converted to the state of perfect gases have values of $p v/T$ whose ratio is exactly 1 : 2. From this law of combining volumes and the basic implication of the molecular theory that substances react by molecules it follows that equal volumes of different perfect gases at the same temperature and pressure, or in general that those quantities of different perfect gases which have equal values of $p v/T$, contain either exactly equal numbers of molecules or numbers of molecules which stand to one another in the ratios of exact integers.

This logical consequence of the law of combining volumes obviously suggests a simpler principle, originally a hypothesis, but later confirmed in so many ways that it is now appropriately regarded as a law. This principle, called *Avogadro's law*, may be stated as follows: Those quantities of different perfect gases which have equal values of $p v/T$ contain an exactly equal number of molecules (*Avogadro, 1811*).

Avogadro's law may also be stated and formulated as follows. The value of $p v/T$ for any quantity of any perfect gas is proportional to the number n of molecules it contains. Representing by k a universal constant (*I, 14*), known as *Boltzmann's constant*, this law is expressed by the equation:

$$p v = k n T. \quad (4)$$

Combination of the equations $p v = n k T$ and $p v = N R T$ gives:

$$n/N = R/k = \tilde{n}, \text{ a universal constant.} \quad (4a)$$

The result expressed by this last equation, which is only another formulation of Avogadro's law, obviously shows that the numbers of molecules $n_A, n_B, \dots$ present in specified quantities of different gases A, B, $\dots$ are directly proportional to the number of mols $N_A, N_B, \dots$ found to be present by applying the perfect-gas equation $N = p v/R T$ to those gases. The equation $n/N = \tilde{n}$ further shows that the same definite number of mole-

cules is present in those different weights of different perfect gases which constitute one mol, empirically defined to be that weight which has the same value of $p v/T$ as do 32 grams of oxygen in the state of a perfect gas. This definite number of molecules per mol of substance is called *Avogadro's number* $\bar{n}$, more descriptively the *mol-molecule number* $\bar{n}$. Its value and that of Boltzmann's constant k , and also the great significance of these quantities in the kinetic molecular theory, will be considered later (III, 12, 13). For present purposes it is important only to note that the *relative* numbers of molecules in different gases are equal to the relative numbers of mols in those gases as derived by the perfect-gas equation from measured values of the pressure, volume, and temperature.

2. Experimental Determination of the Molecular Weights of Gaseous Substances. — Since Avogadro's law affords a measure of the relative number of molecules present in definite weights of various gases, it obviously enables the relative weights of their molecules — their so-called molecular weights — to be determined. The experimental determination of the molecular weight of a gaseous substance usually consists in measuring the volume of a weighed quantity of the substance at an observed temperature and an observed pressure. From the values of the volume and pressure and temperature the number of mols present are calculated with the aid of the perfect-gas equation; and by dividing the weight of the gas by this number of mols the *molecular weight* M of the gas is obtained.

**** Experimental Methods of Determining Vapor-Density and Molecular Weight.***

Prob. 1. — Method of Dumas (1827). — A 115-ml. spherical glass bulb with a wide stem tapering to a point is exactly weighed,

* For the significance of prefixed stars as to the possible omission of portions of the text and of problems see the earlier foot-note (I, 1).

In general, experimental methods are outlined in this book only when they are essential to a concrete realization of the concepts under consideration, or when they afford, as in this case, application of the theoretical principles in the form of thought-stimulating problems. Students who take a laboratory course in which such methods are carried out will naturally omit the corresponding problems. For students who are not taking such a laboratory course a lecture demonstration of the apparatus and of the experimental procedure will greatly help to give an appreciation of the methods, as well as of the problems in the book, which may then be assigned as quantitative applications of the lecture demonstrations.

and into it is introduced about 1 ml. of liquid benzene (which boils at 80.3°). The bulb is immersed in a bath of boiling water, with only the tip of the stem protruding; and, when vapor no longer escapes, the tip is sealed. The sealed bulb is cooled, dried, and accurately weighed. The tip is then broken off below the surface of pure water at 20° ; and the bulb, now filled with water, is approximately weighed. In a certain experiment the following data were obtained:

Weight of bulb open to the air 29.1840 g.

Weight at 23° of sealed bulb containing benzene . . . 29.3458 g.

Atmospheric pressure at time of sealing and weighing 760 mm.

Weight of bulb filled with water of density 0.998 . . . 144.1 g.

a. Calculate the volume of the bulb, neglecting the expansion of the glass between 20° and 100° . *b.* Correct the weight of the sealed bulb to a vacuum by the principle that an immersed body is buoyed up by the weight of the fluid which it displaces. *c.* Calculate the density of benzene vapor at 100° and 1 atm. *d.* Calculate the molecular weight of the benzene vapor under the assumption it conforms to the perfect-gas laws. *e.* Find the percentage deviation of this value from that corresponding to the formula C_6H_6 . *Ans. e, + 2.0%.*

Prob. 2. — Method of Hofmann (1868). — A graduated tube 80 cm. long, closed at one end, is filled with mercury and inverted in an open vessel of mercury. The tube is entirely surrounded by a glass jacket through which is passed steam made by boiling water under the barometric pressure. Into the vacuum above the mercury column is introduced 0.1035 g. of a volatile liquid. The mercury column falls till it stands 260 mm. above the mercury-level in the vessel below; and the volume of the completely vaporized liquid is observed to be 62.0 ml. The barometric pressure at the time is 760 mm. At 100° the density of mercury is 13.35, and its vapor-pressure is negligible. *a.* Make a sketch showing the apparatus. *b.* Calculate the density of the vapor. *c.* Calculate the corresponding molecular weight, assuming the vapor is a perfect gas.

Prob. 3. — Air-Displacement Method of Victor Meyer (1878). — A cylindrical bulb provided with a long stem is filled with dry air; and it is heated, while still open to the atmosphere, to a constant temperature (of about 218°) within a vertical jacket filled with vapor of boiling naphthalene. The stem, which protrudes above the vapor jacket, has a side-arm which delivers into a graduated tube filled with water and inverted over water, so that the air to be later expelled from the bulb can be collected and measured. A tiny glass bottle containing 0.2210 g. of a volatile liquid substance is dropped into the heated bulb, and at the same

moment the bulb is cut off from communication with the atmosphere by closing the top of the stem. The liquid rapidly vaporizes, the vapor drives out of the bulb that quantity of air which occupies the same volume at the temperature of the bulb and at the pressure of the atmosphere. This air collected in the measuring apparatus is found to have a volume of 24.65 ml. at 22° under the barometric pressure of 752 mm.; but of this pressure 20 mm. is due to the pressure of water vapor. *a.* Make a sketch showing the apparatus. *b.* State how the quantity of air expelled is related to the quantity of the vaporized substance. *c.* Calculate the number of mols of air expelled. *d.* Calculate the molecular weight of the vapor at the temperature of the bulb, assuming Avogadro's law. *Ans. d, 225.*

Since gases at atmospheric pressure conform to the perfect-gas laws only approximately, and since vapor-densities are commonly determined with much less accuracy than the composition of substances, the exact value of the molecular weight of a compound is usually derived from its gravimetric composition, its vapor-density being employed only to determine what multiple or submultiple of the value so derived is in accordance with Avogadro's law.

Prob. 4. — Exact Evaluation of Molecular Weights. — a. A certain oxide contains exactly 72.73% of oxygen. State what this shows in regard to its molecular weight. *b.* At 0° and 1 atm. one liter of this (gaseous) oxide is found to weigh exactly 1.9770 g. Find the molecular weight of the oxide corresponding to this datum. *c.* Derive the exact molecular weight by considering the data relating both to the composition and the density. *d.* Find the percentage deviation of the observed density from that required by the perfect-gas equation. *Ans. d, 0.68%.*

3. Derivation of the Atomic Weights of Elements and of the Molecular Formulas of Gaseous Compounds. — The exact values of atomic weights are based on analytical determinations of the combining weights (I, δ). The multiple of the combining weight which is the *atomic weight* has been derived for many of the elements by finding the smallest weight of the element contained in one molecular weight of any of its gaseous compounds.* This is the true atomic weight only in case some one of the com-

* More generally stated, the atomic weight of an element may be derived by finding the greatest common divisor of the weights of that element contained in one molecular weight of its various gaseous compounds; but this more complicated relation has seldom, if ever, been needed.

pounds studied contains in its molecule a single atom of the element; and the adopted atomic weight is therefore strictly only a maximum value, of which the true atomic weight may be a submultiple. The probability that the true atomic weight has been found evidently increases with the number of the gaseous compounds whose molecular weights have been determined.

The multiples of the combining weights adopted as the atomic weights have, however, not been derived solely from molecular weights. From the laws relating to the heat-capacities of crystalline and gaseous substances and from other relationships there have been derived independent values of the atomic weights which confirm and extend those obtained from molecular weights.

The *molecular formula* of a gaseous substance, that is, the formula showing the nature and number of the atoms in its molecule (*I*, 8), can evidently be derived from its molecular weight, its composition by weight, and the atomic weights of the elements it contains.

Derivation of Atomic Weights and Molecular Formulas.

Prob. 5. — Oxygen as the Basis of Atomic and Molecular Weights. — Certain oxygen compounds have molecular weights *M* (referred to that of oxygen as 32) and percentages of oxygen *x* as follows: Sulfur trioxide, $M = 80.07$, $x = 59.95$; water, $M = 18.02$, $x = 88.80$; carbon dioxide, $M = 44.00$, $x = 72.73$. *a.* Find the weight of oxygen contained in one molecular weight of each of these oxides. *b.* State what conclusion as to the atomic weight of the element oxygen can be drawn from these results. *c.* State what this shows as to the number of atoms in the oxygen molecule, and show that it reconciles the standards of reference adopted for the system of atomic weights and for the system of molecular weights (*I*, 4).

Prob. 6. — a. Calculate the combining weight of the element contained in the oxide whose composition was given in Prob. 4a. *b.* What conclusion as to its atomic weight can be drawn from this combining weight and from the molecular weight found in Prob. 4c? *c.* What conclusion can be drawn as to the molecular formula of the oxide?

Prob. 7. — a. The chloride of a certain element is found by analysis to contain 52.50% of chlorine, whose atomic weight is 35.46; and it is found to have at 150° a vapor-density 4.71 as great as that of air at the same temperature and pressure. What conclusion can be drawn from these facts as to the exact atomic

weight of the element? *b.* The hydride of the same element is a gas which contains 5.91 % of hydrogen; and it is found to be produced without change in volume when hydrogen (H_2), whose atomic weight is 1.0078, is passed over the solid elementary substance. What conclusion can now be drawn as to the atomic weight of the element? *c.* What are the simplest molecular formulas of the hydride and of the chloride consistent with these conclusions?

Prob. 8. — A certain hydrocarbon is composed of 92.25 % of carbon and 7.75 % of hydrogen, whose atomic weights are 12.00 and 1.0078, respectively. Its density when in the form of vapor at 100° and 1 atm. is 2.47 times as great as that of oxygen under the same conditions. Calculate its exact molecular weight, and derive its molecular formula.

To pure substances in the liquid and solid states are usually assigned chemical formulas (*I, 8*) that represent their molecules in the gaseous state, since the methods available for judging of the molecular state of liquid and solid substances are not general and do not yield exact quantitative conclusions. Such chemical formulas therefore may not show the molecular species that actually exist in the liquid or solid state. To substances in the dissolved state, however, true molecular formulas can be assigned, since principles are known by which the relative numbers of molecules present in dilute solutions can be experimentally determined (*Chap. IV*); but these molecular formulas may not be identical with those representing the molecules that exist in the gaseous state.

4. Deviations from the Perfect-Gas Laws at Moderate Pressures. — At any definite temperature the deviations from the perfect-gas law, so long as these do not exceed two or three percent, are very nearly proportional to the pressure. This fact is expressed by the following equation, which will be called the *moderate-pressure gas equation*:

$$pv(1 - \beta p) = NRT. \quad (5)$$

In this equation the coefficient β evidently represents the fractional increment $(pv - NRT)/pv$ per unit of pressure of the actual value pv of the pressure-volume product above the perfect-gas value (equal to NRT). The value of this coefficient varies with the nature of the gas, and for a definite gas with the temperature. In general, it is smaller the greater the difference

between the temperature of the gas and the temperature at which the gas liquefies at one atmosphere.

Table I shows the values of the percentage deviation from the perfect-gas equation (that is, the values of 100β) at one atmosphere for various gases at 0° (*I.C.T.*, III, 3),* together with their liquefaction-temperatures at one atmosphere (*I.C.T.*, I, 102, 162).

TABLE I. PERCENTAGE DEVIATIONS FROM THE PERFECT-GAS LAWS AT 0° AND ONE ATMOSPHERE.

Gas	He	H ₂	N ₂	O ₂	CH ₄	CO ₂	NH ₃	SO ₂
100 β	+0.046	+0.061	-0.047	-0.094	-0.22	-0.70	-1.51	-2.4
Liq. temp.	-269°	-253°	-196°	-183°	-161°	-78°	-33°	-10°

Prob. 9. — Evaluation of the Deviation-Coefficient. — a. Calculate the value of the percentage deviation-coefficient 100β for nitrous oxide (N_2O) at 0° from the fact that its density at 0° and 1 atm. is 0.00 197 78 g./ml. *b.* State the magnitude and direction of the percentage error that would be made in calculating by the perfect-gas equation the volume of this gas at 0° and 3 atm.

5. Precise Determination of Molecular and Atomic Weights from Gas Densities. — In recent years, since precise methods of weighing large gas-filled vessels have been developed, exact molecular weights of compounds, and from them exact atomic weights of elements, have been derived from gas densities by empirical extrapolation to zero pressure, in accordance with the moderate-pressure gas equation (Eq. 5; III, 4).

**** Exact Molecular and Atomic Weights Derived from Gas Densities.**

Prob. 10. — Nitrogen. — One liter of pure nitrogen at 0° weighs at 1 atm. 1.25050 g., and at 0.1 atm. 0.125002 g. *a.* From these data find the exact value of the $p v$ product for one gram of nitrogen at 0° in the state of a perfect gas. *b.* From this result calculate the exact molecular weight of nitrogen gas. *c.* Find the exact atomic weight of nitrogen, considering that its molecule consists of two atoms. *Ans. c.* 14.007.

* Tabulated data taken from "International Critical Tables" (1926-1930) are indicated by references like the above, which give also the volume and page where the data are recorded.

Prob. 11. — Hydrogen Bromide and Bromine. — Gaseous hydrogen bromide (HBr) at 0° has at various pressures the following densities:

Pressure in atm.	1.0000	0.6667	0.3333
Density in g/l.	3.6444	2.4221	1.20731

a. Find by extrapolation the ratio of density to pressure at zero pressure, and calculate a precise value of the molecular weight of hydrogen bromide. *b.* Find a precise value of the atomic weight of bromine, taking that of hydrogen as 1.0078; and tabulate this beside the value (79.92) obtained by chemical methods.

6. Molecular Formulas of Elementary and Compound Substances. — Knowledge of the molecular formulas of substances, derived from gas densities as above described, is a valuable aid in interpreting their physical properties; but this knowledge is of primary importance because upon it rests the development of the valence concept and of structural formulas, which express in a remarkable way many chemical relationships of substances. Thus the wonderful structure theory of organic chemistry was adequately developed (*Kékulé, 1858*) only after true atomic weights and molecular formulas became known.

The molecular formulas of individual substances are considered in detail in the study of organic and inorganic chemistry. A few of the more general results, especially in the case of elementary substances, are, however, here presented.

It has been found that the molecule of an elementary substance is not necessarily identical with its atom, as was long assumed (1808–1858), but that its molecule often consists of two atoms (*Cannizzaro, 1858*), and sometimes of a still larger number of atoms. The diatomic and polyatomic molecules of elementary substances dissociate progressively into simpler molecules when the temperature is sufficiently increased.

These facts are illustrated by Table II, which shows the number of atoms in the molecules of nearly all of the elementary substances whose gas densities have been determined. The ranges of temperatures given in the first column are those within which the substance at or above its boiling-point and at a pressure of one atmosphere exists mainly in the indicated molecular form or forms. The temperatures given are only rough approximations, and some of the polyatomic forms (such as Se_8 and Sb_4) are uncertain. The Table is intended only for general orientation.

TABLE II. MOLECULES OF GASEOUS ELEMENTARY SUBSTANCES.

<i>Temperatures</i>	<i>Molecular Formulas</i>
All	He, Ne, A, Kr, Xe, Rn.
All	Na, K, Ag; Zn, Cd, Hg; Tl; Pb.
Below 2500°	H ₂ , O ₂ , N ₂ , F ₂ .
Below 800°	Cl ₂ , Br ₂ , I ₂ ; P ₄ , As ₄ ; Se ₈ and Se ₂ .
Below 500°	S ₈ and S ₆ .
800°–1800°	Cl ₂ , Br ₂ and Br, I ₂ and I.
800°–1800°	P ₄ , P ₂ , and P; Sb ₄ and Sb ₂ ; S ₈ and S ₂ .
1800°–2500°	Cl ₂ and Cl, Br, I; P, S ₂ and S, Te ₂ and Te; Bi ₂ and Bi.

With respect to gaseous compound substances the general statement can be made that on the whole their molecules are remarkably simple. Thus nearly all gaseous compounds, except those of carbon, silicon, and boron, have been found to have molecules which contain only one or two atoms of at least one of the constituent elements. This is exemplified by the molecular formulas: OH₂, PCl₃, ClO₂, PF₅, WCl₆, IF₇, OsO₄; and O₂H₂, S₂Cl₂, N₂H₄, N₂O₅, Al₂Cl₆, Cl₂O₇. There are known, however, a few gaseous compounds, other than those of carbon, silicon, and boron, with more complex molecules, such as As₄O₆ and Ge₃H₈.

7. Dalton's Law of Partial Pressures. — The pressure p of a mixture of substances in the gaseous state is presumably the sum of the pressures p_A , p_B , ... of the separate chemical species A, B, ... (I, 8). The pressures of the separate species are called their *partial pressures*.

Partial pressures can be directly measured in cases where a *semipermeable wall*, that is, a wall permeable for only one of the species present in the gaseous mixture, can be found. For example, when a platinum bulb containing a mixture of hydrogen and nitrogen at a high temperature is immersed in a vessel of hydrogen the nitrogen does not pass through the platinum walls, but the hydrogen does so until its pressures within and without the bulb become equal. The difference then observed between the pressure of the mixture within the bulb and the pressure of the hydrogen outside is due to the nitrogen, and this difference is equal to the partial pressure of the nitrogen in the mixture.

Since it is only rarely possible to realize semipermeable walls and to measure partial pressures directly, it is important

that a principle was early discovered (*Dalton, 1805*) by which partial pressures can be calculated in the case of any gaseous mixture whose total pressure is small. This principle, known as *Dalton's law of partial pressures*, states that each chemical species in a perfect-gas mixture has the same pressure as it would if it were alone present in the volume occupied by the mixture.

Dalton's law, when combined with the equation of state for perfect gases, is evidently expressed by the equations:

$$p_A = N_A R T/v; \quad p_B = N_B R T/v; \quad \dots \quad (6)$$

$$p_A = c_A R T; \quad p_B = c_B R T; \quad \dots \quad (7)$$

In the last equations the symbols $c_A, c_B, \dots$ represent the molal concentrations of the respective chemical species. From these equations it obviously follows that the perfect-gas equation $p v = N R T$ or $p = c R T$ is applicable also to mixtures, provided N is understood to mean the sum (ΣN) of the number of mols and c the sum (Σc) of the molal concentrations of all the chemical species present.

Dalton's law shows that the partial pressure ($p_A, p_B, \dots$) of any chemical species in a perfect-gas mixture is equal to the total pressure (p) of the gas multiplied by the ratio of the number of mols ($N_A, N_B, \dots$) of that species to the total number of mols (ΣN) in the mixture. That is, $p_A = p (N_A/\Sigma N); p_B = p (N_B/\Sigma N); \dots$. Calling the ratio $N_A/\Sigma N$ for any species A the *mol-fraction* X_A of that species in the mixture, Dalton's law shows also that the partial pressure of any species in a perfect-gas mixture is equal to the product of its mol-fraction by the total pressure. That is:

$$p_A = X_A p; \quad p_B = X_B p; \quad \dots \quad (8)$$

Dalton's law in the fundamental form which states that the partial pressures of the separate species are independent of one another becomes exact only as the total pressure of the gas approaches zero; but, like the laws of perfect gases applicable to pure substances, Dalton's law and therefore the equations $p_A = c_A R T, \dots$ presumably hold true approximately when applied to gaseous mixtures whose total pressure does not greatly exceed one atmosphere — namely, with a degree of accuracy roughly corresponding to the deviations cited in Table I (*III, 4*).

Air affords an important illustration of partial-pressure considerations. Pure dry air has at different times and places a fairly constant composition: namely, it contains approximately 21.0 mol-percent of oxygen (O_2), 78.0 mol-percent of nitrogen (N_2), 0.94 mol-percent of argon (A), and 0.03 mol-percent of carbon dioxide (CO_2); and, in accordance with Dalton's law, the partial pressures of these four substances in air are 21.0, 78.0, 0.94, and 0.03 percent, respectively, of the total pressure of the air.

The chemical importance of partial pressures arises mainly from the fact (considered in detail in later chapters) that it is the partial pressures of the separate species, not the total pressure of the mixture, which determines the conditions of physicochemical and chemical equilibria. Thus it is not the total pressure of the air but the partial pressures of the oxygen, nitrogen, argon, and carbon dioxide which determine the quantities of these four substances that dissolve in water when it is shaken with air; and it is the partial pressure of the oxygen which determines the equilibria of oxidation reactions occurring in air.

Applications of the Law of Partial Pressures to Industrial Processes.

Prob. 12. — Bessemer Steel Production. — A Bessemer converter is charged with 10 000 kg. of iron containing 3 % of carbon. *a.* Find how many cubic meters of air at 27° and 1 atm. are needed for the combustion of all the carbon, assuming one fifth to burn to CO_2 and four fifths to CO . *b.* Find the partial pressures (in mm.) of the gases evolved.

Prob. 13. — Sulfur Dioxide Production. — In making sulfur dioxide (for use in manufacturing sulfuric acid) under certain operating conditions 30 kg. of sulfur were charged into each burner per hour, and such an excess of air was introduced (to insure complete combustion) that a gaseous mixture containing 10 mol-percent of oxygen resulted. Calculate how many cubic meters of air at 20° and 1 atm. must have been introduced per hour. *Ans.* 205.

Prob. 14. — Producer Gas Manufacture. — Producer gas is made by passing dry air over hot coke. Under certain conditions of operation 92 % of the oxygen was converted into CO and the remainder into CO_2 . *a.* Calculate the volume of the producer gas obtained per unit-volume of air measured at the same temperature and pressure. *b.* Calculate the mol-fractions of N_2 , A, CO , and CO_2 in the resulting gas. *c.* Calculate the actual volume at 20° and 1 atm. of the producer gas obtained per kilogram of carbon burned. *Ans. c,* 5930 l.

8. Determination of the Molecular State of Substances in Gaseous Mixtures. — Just as in the case of a pure gaseous substance at small pressure, so (in virtue of Dalton's law) in the case of a gaseous mixture at small pressure, the total number of mols present in any definite weight of the mixture can be found by applying the perfect-gas equation $p v = N R T$ to measurements of its volume, pressure, and temperature. This knowledge of the number of mols leads in the case of pure substances to determinations of their molecular weights and molecular formulas in the gaseous state (III, 3). In the case of simple mixtures this knowledge is often used to determine the proportions in which there are present the different chemical species (consisting of particular kinds of molecules) that may be produced by a chemical reaction in the gaseous state at higher temperatures out of a pure solid or liquid substance that can be weighed out at room temperature. For example, in the case of iodine, the extent has been determined to which at higher temperatures the diatomic molecules, which predominate at low temperatures, are dissociated into monatomic molecules by the reaction $I_2 = 2I$.

In this way, from the number of mols derived from vapor-density measurements, the qualitative data given in Table II in regard to the molecular formulas of elementary substances were obtained, and in many cases fairly exact quantitative values of their degrees of dissociation were determined. This method has been extensively used also for determining the dissociation of compounds in the gaseous state; thus of $2NO_2$ into $2NO$ and O_2 , of $2SO_3$ into $2SO_2$ and O_2 , of PCl_5 into PCl_3 and Cl_2 , and of N_2O_4 into $2NO_2$.

In general, pressure or volume measurements may evidently be used to determine the equilibrium conditions or the rate (if not too rapid) of any reaction of a type that is attended by a change in the number of molecules present in the gaseous mixture. This type includes, besides reactions of dissociation, reactions of synthesis or polymerization, such as $C_2H_4(g) + H_2(g) = C_2H_6(g)$, or $2C_2H_4O_2(g) = (C_2H_4O_2)_2(g)$, and certain metathetic reactions, such as $C(s) + H_2O(g) = CO(g) + H_2(g)$. On the other hand, this method obviously cannot be employed for studying the rate or equilibrium of a reaction such as $2HI(g) = H_2(g) + I_2(g)$.

Prob. 15. — Molecular State of an Elementary Vapor under Different Conditions. — The density of antimony vapor at 1 atm. has been found at 1572° to be 12.43 times, and at 1640° to be 11.25 times that of air at the same temperature and pressure. *a.* Calculate from each of these data the number of mols that result from 1 fwt. of antimony (1 Sb). *b.* Making the assumption that the only molecules of antimony present are those having the formulas Sb_4 and Sb_2 , calculate the mol-fraction of each kind of molecule present in the vapor at each temperature. (Note that the result would be incorrect if other molecules, such as Sb_3 or Sb, are actually present.)

Prob. 16. — Measurement of the Dissociation of a Gaseous Compound. — A balloon filled with nitrogen tetroxide at 50° and 500 mm. weighs 71.981 g.; the same balloon when evacuated weighs 71.217 g., and when filled at 25° with water (whose density is 0.997 at 25°) weighs 555.9 g.; all these weights being corrected for air-buoyancy. *a.* Calculate the total number of mols of gas present in the balloon. *b.* Calculate the ratio of this number of mols to the number of formular weights of N_2O_4 taken. *c.* Considering that the excess arises from the dissociation $\text{N}_2\text{O}_4 = 2\text{NO}_2$, calculate the percentage 100 γ of the total nitrogen tetroxide that is so dissociated. *d.* Calculate the partial pressures of the N_2O_4 and of the NO_2 which together make up the total pressure of 500 mm. in the balloon. *Ans.* 313 mm. for NO_2 .

II. THE KINETIC THEORY IN GENERAL AND ITS APPLICATION TO GASES AT SMALL PRESSURES.

9. The Fundamental Kinetic Hypotheses. — The molecular theory has, with the aid of certain hypotheses in regard to the motion of molecules, been developed into a body of principles collectively known as the *kinetic theory*. The *fundamental kinetic hypothesis* underlying this theory is that the molecules of fluid (gaseous or liquid) substances are continually in motion in all directions, and that the motions take place in accordance with the ordinary laws of mechanics (*Clausius, 1857*). The molecules frequently collide with one another and with the walls of the containing vessel. This results in a constant interchange of their individual momenta, and consequently in a variation of their velocities from zero up to values much greater than the mean value. This mean value, however, undergoes no change as a result of the collisions, since these are attended by no dissipation of the energy in the form of heat or radiation to the surroundings — a condition commonly expressed by the statement that the collisions are *elastic*.

It is a corollary from this fundamental hypothesis that the *pressure* exerted by the substance on the wall of the containing vessel results from the collisions of the molecules against the wall; or more specifically, that the pressure is the integrated effect of the impacts of the molecules that strike unit-surface of the wall in unit-time.

A highly important theorem relating to *temperature* can also be derived from the fundamental kinetic hypothesis with the aid of the laws of mechanics. This theorem, here called the *kinetic temperature theorem*, states that at the same temperature the molecules of different fluid substances, whatever be their aggregation-state, pressure, or molecular weight, have the same mean value of the *translational kinetic energy*, that is, of the energy which they have in virtue of their linear motions, as distinct from their rotary motions or internal vibrations. Therefore, for different fluid substances A, B, ... with molecules of different kinds having masses $m_A, m_B, \dots$ and velocities $u_A, u_B, \dots$ it is true at any definite temperature that:

$$\frac{1}{2} m_A u_A^2 = \frac{1}{2} m_B u_B^2 = \dots \quad (9)$$

It is to be understood that the translational kinetic energies here considered are the mean values for all the molecules of each substance, and that the velocities $u_a, u_b, \dots$ are those that correspond to these mean kinetic energies. That is, this velocity u is equal to the square-root of the mean of the squares of the individual velocities u_i for all the n molecules of any one kind present; so that:

$$u = \sqrt{\Sigma u_i^2/n}. \quad (10)$$

It will be seen later (III, 19) that this *root-mean-square velocity* u differs by a constant factor from the *average velocity* $\bar{u}$ of the individual molecules,* which equals $(\Sigma u_i)/n$.

The kinetic temperature theorem is also expressed by the statement that the mean translational kinetic energy of the molecules (which increases with the temperature) is determined solely by the temperature. That is,

$$\frac{1}{2} m u^2 = f(T), \text{ identical for all fluid substances.} \quad (11)$$

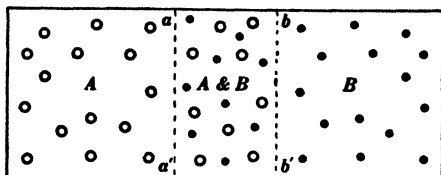
**** Derivation of the Kinetic Temperature Theorem.**

A derivation of the kinetic temperature theorem has been based (*Boltzmann, Bryan, 1894*) on a combination of the two following considerations. First, it was early shown (*Maxwell, 1860*) that the laws of statistical mechanics require that upon mixing two different gases the mean translational kinetic energies of the two kinds of molecules, however different these energies may be in the separate gases, soon become equal to one another in consequence of the interchange of momenta resulting from the collisions of the molecules. Second, it will now be shown, with the aid of this principle, that in two separate gases the mean kinetic energies of the two kinds of molecules are equal when, and only when, their temperatures are equal. For it will be seen that in this case, and only in this case, is it true that no transfer of energy can take place between the two separate gases, which is what *equality of temperature* signifies.

Consider namely that two gases A and B are brought into communication by an arrangement like that shown in Fig. 1.

* In kinetic-theory treatments average or mean values of molecular quantities are often represented by overlining the symbol of the quantity. In this book, where bars above a letter are mainly used to denote specific values of a quantity (*I, 10*), the two meanings are distinguished by using a heavy bar for specific values and a light bar for average values. Under this convention the root-mean-square velocity would be represented by $(\bar{u})^\dagger$; but, because of the frequent occurrence of this fundamental quantity, it is here denoted by the single letter u .

FIGURE 1. ENERGY EQUALIZATION.



In this arrangement, which is assumed to be heat-insulated from the surroundings, an (originally empty) central chamber $aa'b'b$ is separated on one side from the pure gas A by a (semipermeable) wall aa' (*III*, γ) permeable only for the molecules of gas A, and on the other side from the pure gas B by a wall bb' permeable only for the molecules of gas B. In the intermediate chamber, therefore, the two gases will mix; and in this mixture the mean kinetic energies of their molecules will be equalized in case they are unequal in the separate gases. For definiteness assume that in the separate gases $\frac{1}{2} m_A u_A^2$ is greater than $\frac{1}{2} m_B u_B^2$; then in the intermediate chamber the molecules of gas A will by the collisions be decreased in energy and those of gas B increased in energy. The molecules of gas A are, however, continually passing back and forth between the chamber and the vessel containing the pure gas A, and the molecules of gas B between the chamber and the vessel containing the pure gas B, with the result that the gas A decreases in energy and the gas B increases in energy. In other words, there is a transfer of energy from the gas A to the gas B, which is equivalent to saying that the gas A is at a higher temperature than the gas B. And evidently, it is only when $\frac{1}{2} m_A u_A^2 = \frac{1}{2} m_B u_B^2$ for the two separate gases that no such transfer of energy between them would take place; that is to say, only in the case that the mean kinetic energies of the two separate gases are equal would they be at the same temperature.

10. The Kinetic Equation for Perfect Gases. — From the fundamental kinetic hypothesis there may be derived an expression in terms of molecular magnitudes for the pressure-volume product of gases at small pressure. This expression, which will be called the *perfect-gas kinetic equation*, is

$$p v = \frac{1}{3} n m u^2. \quad (12)$$

In this equation n denotes the number of molecules in the volume v of the gas at the pressure p at any definite temperature, m the mass of a single molecule, and u the velocity of the molecules that corresponds to their mean translational kinetic energy at that temperature.

The main considerations underlying this equation are shown by the elementary approximate derivation of it given in Prob. 17. This derivation is not conclusive because it involves the simplifying assumptions that the molecules are all moving in three directions at right angles to one another, and that they are all moving with the same velocity. However, a rigorous analysis leads to the same form of the perfect-gas kinetic equation. Furthermore, such an analysis shows that, as stated above, the velocity u occurring in that equation (Eq. 12), like that occurring in the expression of the kinetic temperature theorem (Eq. 11), is that corresponding to the mean translational kinetic energy of the molecules, and is therefore equal to the square-root of the mean of the squares of the separate velocities of all the molecules (Eq. 10).

Prob. 17. — Approximate Derivation of the Exact Perfect-Gas Kinetic Equation. — A volume v of a perfect gas is contained in a cubical vessel whose edges have the length l . The gas consists of n molecules, each of mass m . Consider for simplicity that the molecules (which actually have varying velocities ranging about a mean value) are all moving with the same velocity u , and that the motions of these molecules, which in reality take place in all directions, are resolved in the three directions perpendicular to the faces of the cube, which is equivalent to assuming that one third of all the molecules is moving in each of these directions.

a. Find the number of impacts which any one molecule makes on the opposite faces in a unit of time. *b.* Find the total number of impacts which all the molecules make on all the faces in a unit of time. *c.* Show that the number of impacts which the molecules make on a unit of surface in a unit of time is $\frac{1}{6} n u/v$. *d.* Find the change of momentum which attends each impact, taking account of the fact that the molecule rebounds from the wall with a velocity equal to that with which it strikes it. *e.* Find the change of momentum of all the molecules that strike a unit of surface in a unit of time. *f.* Noting that this, in accordance with the general equation of mechanics $f = m (du/dt)$, is equal to the force f exerted on the unit of surface or to the pressure, show that the pressure-volume product is expressed by the equation

$$p v = \frac{1}{3} n m u^2.$$

11. Derivation of the Perfect-Gas Laws from the Kinetic Equation. — From the kinetic equation (Eq. 12) Boyle's law, stating that the pressure and volume are inversely proportional, may be immediately deduced. For, since a change only in the

volume of the gas does not cause a variation in the number n of its molecules (unless they are thereby caused to associate or dissociate), and since the mean kinetic energy $\frac{1}{2} m u^2$ of the separate molecules remains constant, in accordance with the kinetic temperature theorem, so long as the temperature remains unchanged, it follows that also the product $p v$ will undergo no change when the volume is varied at a constant temperature.

The law of uniform temperature-effect is also a consequence of the kinetic equation; for any definite change in temperature must evidently cause the same fractional change in the pressure-volume product of different gases, since according to the kinetic temperature theorem it causes the same change in the mean kinetic energy of their molecules.

Also the law of Avogadro is readily derived from the kinetic equation for perfect gases and from the kinetic temperature theorem. For it is evident that for such quantities of two different perfect gases A and B as have equal pressure-volume products at the same temperature, the following relations hold:

$$\frac{1}{3} n_A m_A u_A^2 = \frac{1}{3} n_B m_B u_B^2, \quad \text{since } p_A v_A = p_B v_B.$$

$$\frac{1}{2} m_A u_A^2 = \frac{1}{2} m_B u_B^2, \quad \text{since } T_A = T_B.$$

$$\text{Hence } n_A = n_B. \quad (13)$$

That is, those quantities of different perfect gases which at any definite temperature have equal pressure-volume products consist of an equal number of molecules. — Thus Avogadro's law, originally a hypothesis suggested inductively by the uniform physical behavior of gases and more definitely by the law of combining volumes (*III, 1*), has now been deductively derived from the kinetic theory.

12. Number and Mass of Molecules. — Of great importance in the development of the kinetic theory is a knowledge of the number of the molecules in any given quantity of a gas and of the mass of the individual molecule.

The number of molecules in one mol of any substance or of atoms in one atomic weight of any element (thus of the molecules in 32.00 grams of oxygen or of the atoms in 16.00 grams of the element oxygen) is a universal constant called *Avogadro's number* $\tilde{n}$ (*III, 1*). The value of Avogadro's number has been found (as described below) to be 6.066×10^{23} molecules per mol.

The mass of a single molecule of any substance or of a single atom of any element can evidently be found by dividing the molecular weight of the substance or atomic weight of the element by Avogadro's number.

Prob. 18. — The Number and Mass of Molecules. — a. Calculate the pressure at which a gas contains 10^6 molecules per milliliter at 20° . *b.* Calculate the mass of one molecule of hydrogen, and that of one atom of chlorine.

**** Experimental Determination of Avogadro's Number.**

The value of Avogadro's number has been estimated by a great variety of methods; but most of these yield only roughly approximate results. The most reliable of the precise methods consists in finding the ratio F/e of the most carefully measured value of the quantity of electricity F that passes through a voltaic or electrolytic cell when one atomic weight of silver (107.880 grams) is precipitated or dissolved at its electrodes to the value of the electric charge e on a single electron, determined as previously described (I, 5). Taking 96 490 coulombs as the value of the faraday and 1.5908×10^{-19} coulomb as the value of the electron-charge, the value of Avogadro's number $\tilde{n}$ determined by this method becomes 6.066×10^{23} molecules per mol (Millikan, 1908-1930).*

Another precise method, entirely distinct in principle and involving different kinds of data from the method just described, is based on the determination of the location of atoms in crystals by means of x-rays. Namely, by measuring the angle θ at which a beam of x-rays of known wave-length λ is diffracted from a definite plane of a crystal, such as one of calcite (CaCO_3), the distance l between the parallel planes of atoms lying in that crystal plane can be computed by the simple equation $l = \lambda/2 \sin \theta$. By making such measurements for the various crystal planes all the atoms can be located in a simple crystal, and the number of atoms in unit-volume can be computed. From the density of the crystal, which is the weight of its unit-volume, the total number of atoms in the weight corresponding to any molecular formula (such as CaCO_3), and therefrom Avogadro's number, can be readily found. The method evidently involves exact knowledge of the wave-length of the x-rays used. This is found by measuring the (very small) angles of incidence and diffraction of the x-rays when they fall upon a ruled diffraction-grating.

* The values of the universal constants given here and below (III, 13) are those derived from a critical study of existing data (Birge, 1929, 1932). The value of the electron-charge, here given in coulombs, is 4.769×10^{-10} in electrostatic units.

Avogadro's number determined by this method was found to be about 0.5% lower than the ratio of the faraday to the electron charge given above. This discrepancy has now been removed by the use of a more precise value of the viscosity of air in calculating the electron charge from the oil-drop experiments, — Avogadro's number becoming 6.031×10^{23} (*Millikan, 1938*). Values of related constants given in this text need corresponding revision.

13. Translational Kinetic Energy of Molecules. — For the mean value of the translational kinetic energy of a single molecule at temperature T the following expression is obtained by combining the kinetic equation $p v = \frac{1}{3} n m u^2$ (Eq. 12; III, 10) with the equation $p v = k n T$ (Eq. 4; III, 1) expressing Avogadro's law:

$$\frac{1}{2} m u^2 = \frac{3}{2} k T. \quad (14)$$

Here k is *Boltzmann's constant*, which is equal to the ratio $R/\tilde{n}$ of the gas-constant to Avogadro's number (Eq. 4a; III, 1). Its value has been most exactly derived from that of this ratio, and found to be 1.3706×10^{-16} erg per degree.

Although this relation (Eq. 14) between temperature and kinetic energy was derived from the perfect-gas equations, yet it is applicable to all fluid substances; for, according to the kinetic temperature theorem, the mean kinetic energy of a molecule of a substance is the same function of the temperature, whatever be the nature of the substance and whether its state be that of a perfect gas, an imperfect gas, or a liquid. Therefore, since mean kinetic energy and absolute temperature have been shown (Eq. 12) to be proportional in the case of a perfect gas, they are proportional in the case of any fluid substance. Hence, the kinetic temperature theorem, which was given (in Eq. 11) in the indefinite form $\frac{1}{2} m u^2 = f(T)$, is expressed in definite form by the equation $\frac{1}{2} m u^2 = \frac{3}{2} k T$.

Correspondingly, the total translational kinetic energy $\tilde{E}_T$ of all the molecules in one mol of any fluid substance is evidently given by the expressions:

$$\tilde{E}_T = \frac{1}{2} \tilde{n} m u^2 = \frac{1}{2} M u^2 = \frac{3}{2} R T. \quad (15)$$

Prob. 19. — Kinetic Energy of Molecules. — *a.* Calculate the translational kinetic energy in ergs and calories of the molecules in one mol of any fluid substance at 20° . *b.* Show that the increase in this kinetic energy per degree is 2.980 cal.

14. Velocity of Molecules and Their Impacts on Surfaces.—The equations for the kinetic energy of molecules (Eqs. 14, 15), solved for the (root-mean-square) velocity of the molecules (in any fluid state), become:

$$u = \sqrt{3 k T / m}. \quad (16); \quad \text{or} \quad u = \sqrt{3 R T / M}. \quad (17)$$

An effect that is determined by the concentration and velocity of the molecules, which is of importance in the kinetic treatment of surface phenomena, is the *frequency of impacts* of the molecules upon unit-area of surface. For the number of impacts on the wall per square centimeter per second the expression $\frac{1}{6} u n/v$ was incidentally obtained in the approximate derivation of the kinetic perfect-gas equation (Prob. 17); but a rigorous derivation, which takes into account the fact that the molecules have unequal velocities and that they approach the surface not only normally but obliquely in all directions, shows that the actual number of molecule-impacts z per square centimeter per second is given by the expression:

$$z = \frac{u(n/v)}{\sqrt{6}\pi} = 0.230 u n/v. \quad (18)$$

From Eqs. 18, 12, and 16 or 17 may be derived the following expression for the number of molecules z , and for the number of mols Z , impinging on a square centimeter of surface per second:

$$z = \frac{p}{\sqrt{2} \pi m k T} \quad (19); \quad \text{or} \quad Z = \frac{p}{\sqrt{2} \pi M R T}. \quad (20)$$

These expressions have important chemical applications in the interpretation of the rate of gaseous reactions taking place catalytically on the surfaces of solid substances.

Prob. 20.—*The Velocity of Molecules.*—*a.* Calculate the velocity of hydrogen molecules at 20° and at 100° in centimeters per second and in miles per second (one mile being 1.61 km.).

Prob. 21.—*Number of Molecule-Impacts.*—Derive Eqs. 19 and 20 from previously derived relations.

Note.—The fact that the larger number of impacts obtained by the rigorous derivation does not affect the final form of the kinetic equation arises from compensation, since the change in momentum per impact has (owing to the oblique impacts) a correspondingly smaller value than the mean value given by the expression $2 m u$ found in the approximate derivation.

**** 15. Rate of Effusion of Gases.**—A phenomenon closely related to the velocity of molecules and to the number of them that reach unit-surface in unit-time is the rate at which a gas flows through a small hole in a thin wall or through a small short tube, or through a porous diaphragm (consisting of a congeries of such holes or tubes), between two bodies of the gas at different pressures. This flow phenomenon in any of its various forms is called *effusion*.

The principles governing the rate of effusion are, from the view-points of this book, significant in two respects: first, fundamentally, because they afford a simple and direct experimental confirmation of the kinetic theory; and second, chemically, because they furnish a new method of determining the molecular weights of gases and because they suggest a process of fractionating mixtures of gases of different molecular weights.

**** Confirmation of the Kinetic Theory by the Effusion of Low-Pressure Gases.**

The simplest kinetic conditions are realized when the two bodies of the gas communicate through a small hole in a thin wall and when they have such small pressures that the diameter of the hole is smaller than the average distance traversed by the molecules between their collisions with one another—that is, than the distance commonly called their mean free path (III, 16). Under these conditions it can be shown that the number of molecules or of mols effusing through the hole is equal to the difference in the number of molecules or of mols that would reach the two opposite surfaces of the hole in case it were covered. Expressions for the number of molecules and mols impinging upon unit-area of a surface from within a body of a perfect gas have, however, already been given (Eqs. 19, 20; III, 14). Therefore there may at once be written down the following expression for the number of mols N_{eff} of a perfect gas having a temperature T and molecular weight M effusing in time t through a small hole of area a in a thin wall separating two bodies of the gas at the (small) pressures p_1 and p_2 :

$$N_{\text{eff}} = \frac{(p_1 - p_2) a t}{\sqrt{2} \pi M R T}. \quad (21)$$

This expression shows that the number of mols effusing per second through the same hole in the case of the same gas should be inversely proportional to the square-root of its absolute temperature, and in the case of different gases should be inversely proportional to the square-root of their molecular weights. These conclusions

have in fact been confirmed by careful experiments made with oxygen at 22° and 100°, and with hydrogen, oxygen, and carbon dioxide at 22°.

Of far greater significance, however, is the fact that the absolute number of mols of gas effusing has been found to be in close agreement with the requirements of the kinetic theory as expressed by Eq. 21. Namely, effusion-rate experiments have been made at 22° under conditions eliminating so far as possible secondary effects, thus with a hole (in very thin platinum foil) having an area of 5.2×10^{-6} sqcm. and with a gas at a pressure less than 0.15 mm. on one side and at zero pressure on the other side of the wall; and these experiments (after correcting for secondary effects) led to observed values of the specific effusion-rate, equal to N_{eff}/pat , which compare with the values calculated by Eq. 21 as shown in the following table (*Knudsen, 1909*):

	Hydrogen	Oxygen	Carbon Dioxide
Observed value $\times 10^7$	17.5	4.42	3.63
Calculated value $\times 10^7$	17.9	4.49	3.85

This concordance of the observed and calculated values is probably the most direct proof that exists of the substantial correctness of the developments of the kinetic theory presented in preceding articles.

***** Molecular Weights of Gases Determined from Their Rates of Effusion.***

Measurements of the effusion-rate of gases at low pressures through small holes in thin walls have been used for determining (with the aid of Eq. 21) the relative molecular weights of gases.

There are, however, other types of effusion whose rates are less simple theoretically, but are more readily studied experimentally, for which the same inverse proportionality between the rate and the square-root of the molecular weight prevails. Thus this has been found to be true of the molecular flow of gases through diaphragms of porous materials like gypsum or meerschaum (*Graham, 1829*). By considering such diaphragms to consist of a multitude of very narrow short tubes with whose walls the molecules collide and from which they are thrown back at random in all directions, it has been shown (*Knudsen, 1909*) that the kinetic theory leads to the conclusion that the effusion-rate should be proportional for a given diaphragm to the difference of pressure on the two sides and inversely proportional to the square-roots of the absolute temperature and of the molecular weight of the gas, just as in the case of effusion through a small hole in a thin wall (Eq. 21).

The relative rates of effusion of different gases at larger pressures (such as that of the atmosphere) through a short capillary tube were early stated (*Bunsen, 1857*) to be inversely proportional to their densities or molecular weights; and this principle is sometimes still employed, especially in technical practice, for deriving the relative densities of gases from measurements of the time-intervals during which equal volumes of air and of other gases escape through the same tube under the same difference in pressure. This phenomenon is, however, one of mass flow, not of molecular flow—one determined by the laws of aerodynamics, not by the principles of the kinetic theory; and it is related to the energies involved in the flow of fluids, rather than to the velocities and masses of their molecules. Moreover, these aerodynamic laws of mass flow show that the relative rates of effusion under the conditions here considered, even in case of perfect gases, depend not only on the densities but also on the heat-capacities of the gases. Also investigation shows that the rates are affected by many secondary influences; so that the Bunsen method of determining the densities of gases is an inexact and unreliable one (*Buckingham, Edwards, 1919*).

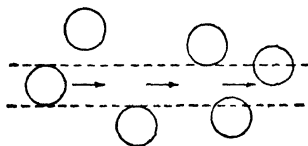
16. Collisions, Mean Free Path, and Size of Molecules.—Some characteristics of molecules related to their dimensions will be now considered. The most important of these are: (1) the cross-section of the molecules, considered to be spherical; (2) the number $\bar{z}$ of the collisions per second between all the molecules ($\bar{n}$ in number) that are present in one cubic centimeter of gas at any specified pressure and temperature; and (3) the average distance traversed by a molecule between its collisions, called the *mean free path* $\bar{l}$. Knowledge of these molecular magnitudes is essential in the kinetic interpretation not only of many physical properties, but also of the rate of chemical reactions, whose adequate treatment constitutes one of the major problems of chemistry.

Approximate relations between these three quantities can be derived (Prob. 22) by making the simplifying assumption that each individual molecule in turn is moving at a definite velocity u and that all the other molecules among which it is moving are stationary. Nearly exact relations can be derived by considering that all the molecules are simultaneously moving at the same uniform velocity u corresponding to their mean kinetic energy $\frac{1}{2} m u^2$ (*Clausius, 1858*). Rigorous expressions have been obtained (*Maxwell, 1860*) by taking into account the

actual condition that the molecules are moving with different velocities varying around the value u in accordance with Maxwell's distribution law (III, 19).

Prob. 22. — Approximate Relation between the Number of Collisions and the Cross-Section of Molecules. — Consider, as illustrated by Fig. 2, that a molecule of diameter d is moving with a velocity u through a gas containing in each cubic centimeter $\bar{n}$ stationary molecules of the same kind. Derive expressions for: a , the volume of the space within which the centers of the stationary molecules must be located in order that the moving molecule may collide with those molecules during one second; b , the number of collisions z which one moving molecule makes with the stationary

FIGURE 2. MOLECULE COLLISIONS.



molecules each second; c , the total number of collisions $\bar{z}$ made per second by all the $\bar{n}$ molecules in one cubic centimeter. (Consider that each of the molecules becomes in turn the moving molecule, and note that the factor $\frac{1}{2}$ has to be introduced to avoid counting twice the collisions between each pair of molecules, for example, to avoid counting as two separate collisions that of a molecule A with a molecule B and that of the molecule B with the molecule A.) *Ans.* $\bar{z} = \frac{1}{2} \bar{n}^2 \cdot \pi d^2 \cdot u = 1.571 \bar{n}^2 u d^2$.

Prob. 23. — Relation between the Mean Free Path and the Cross-Section of Molecules. — Defining the mean free path $\bar{l}$ as in the above text to be the average distance traversed by any molecule between its collisions with other molecules, derive a relation between the mean free path and the cross-section πd^2 (four times that of a single molecule) from the expression for the number of collisions made by any one molecule per second found in Prob. 22b. *Ans.* $\bar{l} = 1/(\bar{n}\pi d^2)$.

The exact relations between the number of collisions and the cross-section πd^2 can be rigorously derived, as stated above, by a mathematical analysis in which the simplifying assumption made in Prob. 22 as to the motion of the molecules is replaced by the postulates, corresponding to the actual conditions, that all the molecules are in motion and that their velocities vary around a mean value as required by Maxwell's distribution law. This derivation leads to the following expressions for the number of collisions z per second made by one molecule, and for the number of collisions per second $\bar{z}$, often called the *collision-*

frequency, made by all the $\bar{n}$ molecules present in one cubic centimeter:

$$z = \frac{4}{\sqrt{3}\pi} \bar{n} \cdot u \cdot \pi d^2 = 4.09 \bar{n} u d^2. \quad (22)$$

$$\bar{z} = \frac{2}{\sqrt{3}\pi} \bar{n}^2 \cdot u \cdot \pi d^2 = 2.045 \bar{n}^2 u d^2. \quad (23)$$

Replacing the velocity u by its value $\sqrt{3RT/M}$ (Eq. 17) and then the number of molecules $\bar{n}$ by its value $\tilde{n}c$ (where $\tilde{n}$ is Avogadro's number and c is the molal concentration, here in mols per cubic centimeter), this becomes:

$$\bar{z} = \frac{2}{\sqrt{\pi}} \bar{n}^2 \cdot \pi d^2 \cdot \sqrt{\frac{RT}{M}} = 3.545 \tilde{n}^2 c^2 d^2 \sqrt{RT/M}. \quad (24)$$

It is seen that, as would be expected, the total number of collisions per second is proportional to the cross-section of the molecules, to the square of the number of molecules per cubic centimeter, and to their velocity; or that the total number of collisions per second is proportional to the cross-section of the molecules, to the square of the molal concentration of the gas, and to the square-root of its absolute temperature, and inversely to the square-root of its molecular weight.

The corresponding rigorous expression for the mean free path depends on the method of averaging the free paths of the separate molecules, which have somewhat different free paths because of their different velocities. The results of different methods of averaging differ, however, by only a few percent. Without considering these differences, the following closely approximate expression may be given:

$$l = \frac{0.707}{\bar{n} \pi d^2} = \frac{3.72 \times 10^{-25}}{c d^2}. \quad (25)$$

This equation shows that the mean distance traversed between collisions is inversely proportional to the cross-section of the molecules and to their number per unit-volume, or to the cross-section of the molecules and to the molal concentration of the gas.

It is of interest to note that use of the postulates that all the molecules are in motion and that their velocities are equal changes the value of the numerical coefficient in the expression for the total number of collisions from 1.571 (as found in Prob. 22c)

to 2.094, and that use of the postulate that the molecules have distributed velocities changes this last coefficient from 2.094 to 2.045 (as shown by Eq. 23). It may also be noted that the numerical coefficient in the expression for the mean free path (which was given as 0.707 in Eq. 25) varies with the different methods of averaging only between 0.677 and 0.743 (*Tolman, 1927*, "Statistical Mechanics," p. 219). It should also be stated that Eqs. 22, 23, and 26 are those given by *Herzfeld and Smallwood, 1931*, in Taylor's "Physical Chemistry," pp. 124, 157.

The mean free path is a factor that determines the magnitude of certain measurable properties of gases, especially of their viscosity and their thermal conductivity; and conversely, from the results of measurements of these properties there can be computed the magnitude of the mean free path and of the related molecular magnitudes.

For the determination of the viscosity of gases various experimental methods have been employed. The simplest of these methods, commonly used when only the relative values for different gases are wanted, involves measuring the rate of flow of the gases through a long capillary tube. In another precise method, which is more elaborate but gives absolute values, a vertical cylinder containing the gas is rotated at a known uniform speed, and there is placed within this cylinder concentric with it another smaller cylinder supported by a delicate suspension, so that this inner cylinder turns through a certain (measured) angle till the viscous force exerted upon it by the rotating fluid is balanced by the (independently determined) torsional force of the twisted suspension. From such measurements the value of the so-called *viscosity-coefficient* η is computed (*III, 17*).

From the experimentally determined viscosity-coefficient the mean free path $\bar{l}$ of the molecules of the gas is calculated by the following kinetically derived equation:

$$\bar{l} = \frac{1.256 \eta}{p \sqrt{M/R T}}. \quad (26)$$

Prob. 24. — Calculation of Molecular Magnitudes. — From the viscosity of carbon dioxide gas at 0° and 1 atm. the mean free path of its molecules has been computed to be 3.9×10^{-8} cm. *a.* Calculate the diameter of the carbon dioxide molecule. *b.* Calculate the volume of the molecule, assuming it to be spherical. *c.* Calculate the total number of collisions per second between the molecules in 1 ccm. of carbon dioxide at 0° and 1 atm.

From the diameter of the molecules, found as above, the corresponding *volume* of the molecules, provided these are considered to be spherical as has been assumed, can be derived from geometrical relationships (as in Prob. 24). Of more importance in applications of the kinetic theory is a related quantity, which may be called the *effective volume* of the molecules, since it corresponds to the decrease in the paths of the molecules which, so far as collisions are concerned, results from the actual volume of the molecules. The effective volume can be shown to be four times the actual volume (which is $\frac{1}{6} \pi d^3$). The total effective volume b of the $\tilde{n}$ molecules in one mol is therefore given by the expression:

$$b = \frac{2}{3} \pi d^3 \tilde{n}. \quad (27)$$

The plausibility of this formula may be indicated by calling attention to the fact that the sphere circumscribing two colliding molecules has a volume of $\frac{4}{3} \pi d^3$, whereas the actual volume of two molecules is $\frac{1}{3} \pi d^3$; but the reliability of the expression can be proved only by a rigorous discussion of the effect upon the free paths of the molecules.

It will be seen later that this effective volume b can be derived independently from other kinetic considerations, and that the two methods of derivation lead to numerical values of the same general magnitude.

**** Limited Significance of Molecular Magnitudes.**

The significance of the magnitudes of the diameter, cross-section, and volume of molecules is limited by the following considerations.

In the first place, the assumption that molecules are spherical is undoubtedly usually incorrect, and can be regarded only as a convenient first approximation; thus even the simple molecule of carbon dioxide has been shown (by the structure of its crystals in the solid state and by its spectrum in the gaseous state) to have its three atoms in a straight line, so that the molecule is more nearly cylindrical than spherical.

Secondly and more fundamentally, molecules are not rigid bodies whose distance from one another at the moment of so-called collision is determined by actual contact between physical surfaces. On the contrary, the apparent diameter of molecules corresponding to the experimentally derived mean free path actually means the *average distance of nearest approach* of the

centers of two molecules to one another, and is probably really determined by the following conditions. When molecules get very close to one another, a force of repulsion develops between them (perhaps in part owing to repulsion of the outer electrons of their atoms), and this force destroys the velocity of the approaching molecules and then causes them to recede from one another. This distance of nearest approach, which is the apparent molecular diameter, would therefore be expected, even in the case of two like molecules, to depend upon their momentum or velocity, and therefore to vary with the temperature; and in the case of two unlike molecules in a mixture of gases, it would depend also on the magnitudes of the forces with which these molecules repel one another, and might therefore not be simply related to the diameters which the two kinds of the molecules show in the separate gases.

To emphasize these limitations, molecular diameters and volumes derived from the kinetic theory of gases are sometimes called *gas-kinetic* diameters and volumes.

**** Collisions of Molecules of Different Kinds.**

In the study of the rate of chemical reactions between two or more gaseous substances a knowledge of the number of collisions between the molecules of the different kinds that enter into reaction with one another is of great importance. It may therefore be mentioned that from the kinetic theory there has been derived the following expression for the total number of collisions $\bar{z}$ per second between the $\bar{n}_A$ molecules of a gas A and $\bar{n}_B$ molecules of a gas B present in one cubic centimeter of a gas mixture, in terms of the distance d_{AB} of nearest approach of the two kinds of molecules and of the molecular weights M_A and M_B of the gases:

$$\bar{z} = 2\sqrt{2/\pi} \bar{n}_A \bar{n}_B \pi d_{AB}^2 \sqrt{RT} \sqrt{\frac{M_A + M_B}{M_A M_B}}. \quad (28)$$

It will be seen that, as was to be expected, the number of collisions is proportional to the number of molecules of each substance per cubic centimeter and to the cross-section of an area πd_{AB}^2 corresponding to a radius which is equal to the nearest approach of the centers of the two kinds of molecules. If the molecules be regarded as spheres which collide at definite boundaries, the distance d_{AB} is evidently equal to one half the sum of the diameters of the two kinds of molecules; that is, $d_{AB} = \frac{1}{2} (d_A + d_B)$.

Prob. 25. — Derivation of an Approximate Expression for the Number of Collisions between Two Kinds of Molecules. — Derive by reasoning like that of Prob. 22 an approximate expression for the total number of collisions $\bar{z}$ per second between molecules of two different kinds A and B of which the numbers $\bar{n}_A$ and $\bar{n}_B$ respectively are present in a cubic centimeter of a gas mixture at

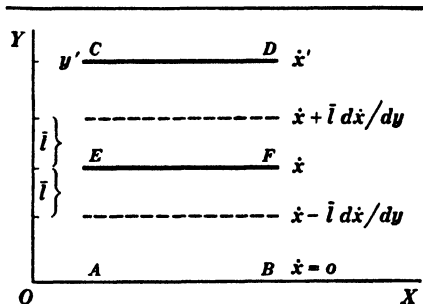
temperature T . Consider first that the A molecules move and that the B molecules are stationary, and second, that the B molecules move and that the A molecules are stationary; and note that the sum of two results must (as in Prob. 22) be divided by two to avoid counting the same collisions twice. Bring the expression into a form like Eq. 28, and tabulate the approximate and exact expressions so as to show their similarities and differences.

**** 17. Viscosity of Gases and its Molecular Interpretation.**—The phenomenon of the viscosity of fluids and the molecular processes from which it arises in the case of gases will be here illustrated, since it affords, as above stated, the most usual method of determining molecular magnitudes.

**** Phenomenon of Viscosity. Definition of Viscosity-Coefficient.**

Consider, as in Fig. 3, that two parallel horizontal plates (in XZ planes), separated by a small distance y' , are immersed in a fluid substance. Consider that the lower plate AB is stationary, and that the upper plate CD is, by a force f steadily applied to it, kept moving at a constant velocity $\dot{x}'$ in the direction of the X axis.*

FIGURE 3. VISCOSITY OF GASES.



It is found experimentally that the velocities of the fluid in the layers adhering to the plates are zero and $\dot{x}'$ respectively, and that, when its flow is steady and non-turbulent, there is a constant velocity-gradient $\frac{d\dot{x}}{dy}$ (equal to $\dot{x}'/y'$) between the two plates. Furthermore, the force f that serves to produce this steady flow is

* This arrangement is an idealized one which evidently corresponds in principle to the concentric cylinders, one rotating and the other stationary, used in the previously described apparatus (III, 16) for measuring the viscosity of gases.

Velocity-components are here and later indicated, as often in mechanics, by placing a dot above the position-coordinate; thus for $u_x = dx/dt$ is written $\dot{x}$.

found to be proportional to the area a of the moving plate and to the velocity-gradient, and to be determined also by the nature and temperature of the fluid.

This frictional resistance of the fluid is called its *viscosity*; and its *viscosity-coefficient* η is defined to be the force per unit-area of the moving plate (in dynes per square centimeter) which produces in the fluid between the plates a velocity-gradient of unity (that is, of one centimeter per second per centimeter). These principles and this definition are expressed by the equation:

$$f/a = \eta \frac{d\dot{x}}{dy}. \quad (29)$$

****Kinetic Molecular Interpretation of the
Viscosity of Gases.**

The molecular interpretation of the viscosity of gases at small pressure will now be presented in broad outline — without attempting an exact or rigorous treatment. Referring again for the sake of definiteness to the conditions represented by Fig. 3, note first the following facts:

(1) When the gas is in a steady state of flow, the force f/a applied to unit-area of the moving plate must be such as to restore to that plate the momentum which is being transferred in unit-time from it to the stationary plate through the gas (since in general $f = d(mu)/dt$).

(2) The transfer of momentum through the gas arises from the passage of its molecules across the horizontal layers of the gas, which passage results from the upward and downward velocity-component (parallel to the Y axis) of the motions of agitation of the molecules. For by these motions some of the directed velocity $\dot{x}$ arising from the mass flow is carried from the faster-moving to the slower-moving layers, and the reverse. (That there may be no appreciable disturbance of the molecular motions of agitation it will be assumed that their velocity-components are very large in comparison with the mass-flow velocity, as in practice is always the case.)

Let us consider now, as shown in Fig. 3, within the gas an ideal horizontal plane EF of unit-area at which the directed mass-flow velocity is $\dot{x}$, and determine the quantity of directed momentum which the upward and downward moving molecules carry through this plane in unit-time. The number of such molecules reaching the plane from below is $\frac{1}{6} \bar{n} u$, and the number reaching it from above is also $\frac{1}{6} \bar{n} u$, under the approximate assumptions that all the molecules (of which the number $\bar{n}$ is present in unit volume) have the uniform value u , and that their motions take place only in directions corresponding to the three rectangular axes (III, 10). Now these molecules reaching the plane have on

an average come from a distance equal to the mean free path $\bar{l}$ above and below the plane since they last collided with other molecules. Through these collisions they acquired the mass-flow velocity prevailing in the respective horizontal layers; and therefore on the average a downwards moving molecule reaches the plane with a mass-flow velocity of $\dot{x} + \bar{l} (d\dot{x}/dy)$, and an upward moving molecule reaches it with one of $\dot{x} - \bar{l} (d\dot{x}/dy)$. Hence, representing by m the mass of a molecule, there results in unit-time a net transfer of mass-flow momentum downward through the (unit-area) plane equal to:

$$\frac{1}{3} m \bar{n} u [(\dot{x} + \bar{l} d\dot{x}/dy) - (\dot{x} - \bar{l} d\dot{x}/dy)] = \frac{1}{3} m \bar{n} u \bar{l} d\dot{x}/dy.$$

Note that this quantity of momentum equals the force f/a applied to the moving plate, since the same quantity of momentum must pass downward from the plate through every horizontal layer of the gas if its state of flow is to remain steady. Noting also that the definition of the viscosity-coefficient (Eq. 29) gives $d\dot{x}/dy = f/a \eta$, that $m \bar{n}$ is the density of the gas, that this for a perfect gas of molar weight M equals $p M/R T$ (Eq. 2; III, 1), and that by Eq. 17 (III, 14) the velocity $u = \sqrt{3 R T/M}$, it will be seen that:

$$\eta = \frac{1}{3} m \bar{n} u \bar{l}; \quad \text{or} \quad \bar{l} = \frac{\sqrt{3} \eta}{p \sqrt{M/R T}}. \quad (30)$$

It will be seen that this relation between the mean free path and viscosity of the gas is identical with the exact expression cited above (Eq. 26), except that the numerical factors $\sqrt{3}$ (equal to 1.732) and 1.256 differ considerably. This difference arises from the inexactness of the approximate assumptions used in deriving Eq. 30.

18. Molecular Magnitudes. — In Table III are presented typical examples of molecular magnitudes derived from the principles described in Arts. 12–16. Specifically, these values were computed from experimental data by the formulas given in the second column of the table, which are identical with or closely related to the equations whose numbers are given in that column.* The volume of the molecules in one mol given in the table is the effective volume b as defined in Art. 16.

* The values given for the mean free path are those computed by Herzfeld and Smallwood (Taylor's "Physical Chemistry," 1, 248; 1931). From these values the diameter of each molecule, the effective volume of the molecules in one mol, and the number of collisions were calculated by the authors of this book by the formulas given in the table.

TABLE III. MOLECULAR MAGNITUDES AT 0° AND ONE ATMOSPHERE.

Quantity	Formula Used for Computation	Values of the Quantity				
		He	A	H ₂	O ₂	CO ₂
Molecular formula of gas	$M = \bar{m} R T / p$ (Eq. 2)	4.00	39.94	2.016	32.00	44.00
Molecular weight of gas	$\bar{m} = F / e$ (Art. 12)	6.06	6.06	6.06	6.06	6.06
Number of molecules in 1 mol	$\bar{n} = \bar{n} p (1 - \beta p) / R T$ (Eq. 5)	2.70	2.71	2.70	2.71	2.72
Number of molecules in 1 ccm.	$m = M / \bar{n}$	0.66	6.59	0.33	5.28	7.26
Mass of one molecule	$u = \sqrt{3 R T / M}$ (Eq. 17)	13.0	4.13	18.4	4.61	3.93
Velocity of molecules	$\bar{l} = 1.26(\eta / p) \sqrt{R T / M}$ (Eq. 26)	17.5	6.2	11.2	6.3	3.9
Mean free path	$d = 0.474 / \sqrt{\bar{l} \bar{n}}$ (Eq. 25)	2.18	3.66	2.72	3.64	4.62
Diameter of each molecule	$b = \frac{2}{3} \pi \bar{n} d^3$ (Eq. 27)	13.2	62.6	25.7	61.1	126
Volume of molecules in 1 mol	$z = 7.09 \bar{n} d^3 \sqrt{R T / M}$ (Eq. 22)	6.8	6.2	15.1	6.8	9.4
Collisions of one molecule per second	$\bar{z} = 3.54 \bar{n}^2 d^2 \sqrt{R T / M}$ (Eq. 24)	9.2	8.3	20.4	9.2	12.7
Collisions of the molecules in one ccm. per second						$\times 10^{28}$ units.
						$\times 10^4$ cm./sec.
						$\times 10^{-6}$ cm.
						$\times 10^{-8}$ cm.
						$\times 1$ ccm.
						$\times 10^9$ units.

From the values in Table III there may be drawn the following general conclusions:

(1) Simple molecules, like those of the substances named in the table, have a diameter of 2 to 5 angstroms (one angstrom being equal to 10^{-8} cm.). The diameter increases slowly with the weight of the molecule, but is not markedly greater for diatomic and triatomic molecules than for monatomic molecules, indicating that the atoms are not widely separated.

(2) The total effective volume of simple molecules is at 0° and 1 atm. from 0.05 to 0.5 percent of the volume of the gas (which is 22 400 ccm. per mol).

(3) The mean free path of the molecules at 0° and 1 atm. is of the order of only 10^{-5} cm. It is 200 to 800 times greater than the diameter of the molecules; but is extremely small in relation to the distance (about 10^5 cm.) traversed by the molecule in a second. This accounts for the fact that gases, under ordinary conditions, in spite of the high velocity of their molecules, diffuse only slowly into one another. It is to be noted, however, that the mean free path is inversely proportional to the pressure of the gas, and therefore that at very small pressures, such as prevail in "vacuum tubes," the distance traversed between collisions may be of the order of the dimensions of laboratory apparatus; thus in oxygen at 0° and at a pressure of 0.01 mm. of mercury the mean free path is about 1 cm.

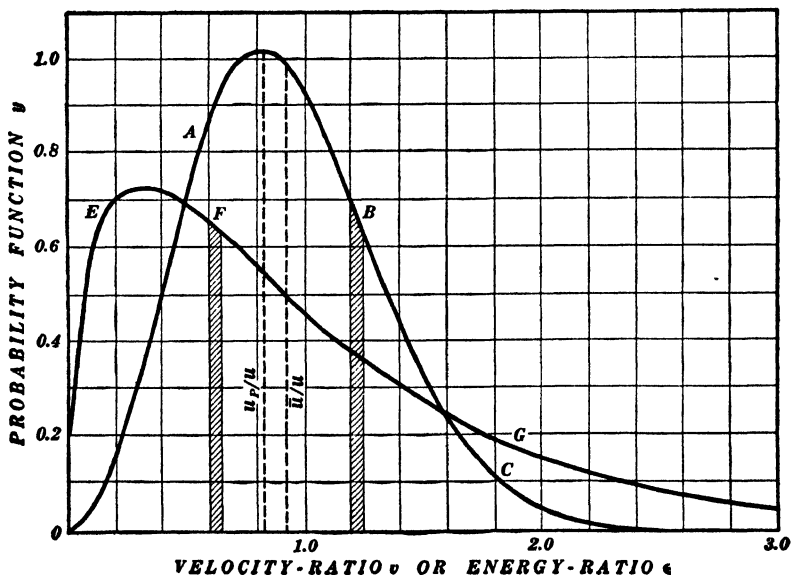
(4) In correspondence with the large velocity of the molecules and their small mean free paths the number of collisions at atmospheric pressure is enormous, thus of the order of 10^{29} per second for all the molecules in 1 ccm. In consequence of these frequent collisions the motion of any one molecule consists of a vast number of short zig-zag paths.

19. Distribution of the Velocities and Translational Kinetic Energies of Molecules. — It has already been stated that the individual molecules of a gas can not all have the same velocity and the same translational kinetic energy; for as a result of the collisions there is a constant interchange of their momenta and kinetic energies, with consequent variation of the values of their velocities and translational kinetic energies from zero up to values much greater than the mean value. The character of this variation will now be considered.

It has been shown (*Maxwell, 1860*) that, because of the very large number of molecules and the frequency of their collisions, their velocities and translational kinetic energies must be distributed in accordance with the statistical laws of probability, of which the distribution of shots around a bull's-eye or errors of observation around the mean value afford illustrations. The law which expresses the fraction of the molecules which at any one temperature have specified velocities or kinetic energies is known as *Maxwell's distribution law*.

Maxwell's law is illustrated by Fig. 4, whose two graphs show the distribution of velocities and the distribution of translational kinetic energies required by that law. Namely, the graph OABC is drawn by plotting points whose abscissas are the values of the ratios v of the velocities u_i of individual molecules to the root-mean-square velocity u of all the molecules, and whose ordinates are the values of the probability function $y' = 4.146 v^2 e^{-1.5 v^2}$, which is the function which when multiplied by an infinitesimal increment dv of the velocity-ratio v gives (in accord with Eq. 31 below) the fraction dn_i/n of all the mole-

FIGURE 4. DISTRIBUTION OF VELOCITIES AND ENERGIES.



cules (n in number) which at any definite moment have velocity-ratios between v and $v + dv$. All the values refer to any one uniform temperature.

Similarly, the graph OEFG is drawn by plotting points whose abscissas are the values of the ratios ϵ of the kinetic energy $\frac{1}{2} m u_i^2$ of individual molecules to the mean value $\frac{1}{2} m u^2$ of the kinetic energies of all the molecules, and whose ordinates are the values of the probability function $y'' = 2.073 \epsilon^{0.5} e^{-1.5 \epsilon}$, which is the function which when multiplied by an infinitesimal increment $d\epsilon$ of the kinetic-energy ratio gives (in accord with Eq. 32 below) the fraction dn_i/n of all the molecules (n in number) which at any definite moment have kinetic-energy ratios between ϵ and $\epsilon + d\epsilon$. Again, all the values refer to any one temperature.

From a geometric view-point the probability-functions y' and y'' are evidently the equations of the curves OABC and OEFG in Fig. 4; and the shaded areas below the letters B and F represent the molecule-fractions dn_i/n , whereas the total areas (equal to unity) below the graphs correspond to the whole number of molecules.

It may also be mentioned that the fraction dn_i/n may be interpreted, not only as above to signify the fraction of all the molecules which at any one time has velocity ratios or kinetic-energy ratios between the specified limits, but also to signify the fraction of the time during which any one molecule has velocity or kinetic-energy ratios between the specified limits.

The corresponding expressions for these molecule-fractions are evidently as follows:

$$\frac{dn_i}{n} = 4.146 e^{-1.5 v^2} v^2 dv. \quad (31)$$

$$\frac{dn_i}{n} = 2.073 e^{-1.5 \epsilon} \epsilon^{0.5} d\epsilon. \quad (32)$$

The numerical factors 4.146 and 2.073 are the values of the coefficients $3\sqrt{6}/\pi$ and $3\sqrt{1.5}/\pi$ which occur in the theoretically derived Maxwell equations.

Except at very low temperatures (where quantum effects enter), these expressions are known to be substantially exact in the case of gases at small pressures, and are commonly regarded as close approximations in the case of other fluid states.

Table IV illustrates the distribution values to which these expressions lead. In the first column are shown the numerical percentages of the molecules which have velocity ratios v (equal to u_i/u) or kinetic-energy ratios ϵ (equal to E_i/E or to u_i^2/u^2) which lie between the limits shown in the second and third columns of the table. These values were obtained by evaluating the integrals of Eqs. 31 and 32 between these limits.

TABLE IV. DISTRIBUTION OF THE VELOCITIES AND TRANSLATIONAL KINETIC ENERGIES OF MOLECULES.*

<i>Percentage of Molecules</i>	<i>Velocity Ratios v</i>	<i>Kinetic-Energy Ratios ϵ</i>
1.4	0.000–0.217	0.000–0.047
8.2	0.217–0.434	0.047–0.188
16.7	0.434–0.651	0.188–0.424
21.4	0.651–0.868	0.424–0.753
20.2	0.868–1.085	0.753–1.177
15.2	1.085–1.302	1.177–1.695
9.2	1.302–1.519	1.695–2.307
7.1	1.519–2.041	2.307–4.166
0.60	2.041– ∞	4.166– ∞
100.0	0– ∞	0– ∞

* Calculated by the authors from data given in O. E. Meyer's "Kinetic Theory of Gases," Baynes' translation, p. 57 (1899), and in Boynton's "Kinetic Theory," p. 31 (1904).

Examination of Table IV shows that by far the larger proportion of the molecules have individual velocities which differ considerably from the root-mean-square velocity; yet that only about two percent of them have values less than 0.2 times or more than 2.0 times the root-mean-square velocity. Nevertheless, the small number of molecules that have large velocities, and correspondingly large kinetic energies, are a predominating factor in determining certain physicochemical and chemical phenomena, such as the vapor-pressure of liquids and the rate of chemical reactions. It is therefore important to note that temperature causes a remarkably large increase in the fraction of the molecules which have velocities or kinetic energies greater than a specified absolute value when this specified value is large. Thus from Maxwell's law (as expressed by Eq. 36 below) it is

found that the fractions n_0/n of the molecules that have kinetic energies greater than certain specified values E_0 have the magnitudes shown in Table V. Namely, the molecule-fractions are there given that have at 0° and at 10° C kinetic energies greater than three values (of E_0) that are equal respectively to five, ten, and twenty times the mean kinetic energy at 0° (which last has the numerical value $\frac{3}{2} \times 273.1 k$, equal to $409.7 k$).

TABLE V. FRACTION OF THE MOLECULES WITH LARGE KINETIC ENERGIES.

Specified Lower Limit E_0	Values of n_0/n		
	At 0°	At 10°	Ratio
$5 \times 409.7 k$	1.82×10^{-3}	2.33×10^{-3}	1.282
$10 \times 409.7 k$	1.38×10^{-6}	2.30×10^{-6}	1.668
$20 \times 409.7 k$	5.88×10^{-13}	16.6×10^{-13}	2.82

The large increase with the temperature of the number of molecules with high kinetic energies is especially striking when it is considered that their mean kinetic energy increases only 1.037 fold between 0° and 10° C.

**** Other Expressions of Maxwell's Law.**

The preceding expressions (Eqs. 31 and 32), which show the fraction of the molecules that have velocity *ratios* between u_i/u and $(u_i+du_i)/u$ or kinetic-energy *ratios* between E_i/E and $(E_i+dE_i)/E$, are not dependent on the temperature. Even more directly related to chemical and physico-chemical phenomena are the corresponding expressions (Tolman, 1927, "Statistical Mechanics") which show the fraction of the molecules that have *absolute* velocities between u_i and $u_i + du_i$ or *absolute* kinetic energies between E_i and $E_i + dE_i$, and which show the variation of this fraction with the temperature. By replacing u by $\sqrt{3 k T/m}$ in Eq. 31 (in accord with Eq. 16), and by replacing E by $\frac{3}{2} k T$ in Eq. 32 (in accord with Eq. 14), the following expressions of this kind result:

$$\frac{dn_i}{n} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{1.5} e^{-(mu_i^2/2kT)} u_i^2 du_i. \quad (33)$$

$$\frac{dn_i}{n} = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT} \right)^{1.5} e^{-(E_i/kT)} E_i^{0.5} dE_i. \quad (34)$$

Of great importance is also the fraction of the molecules that have in any specified direction X absolute velocity-components between $\dot{x}_i$ and $\dot{x}_i + d\dot{x}_i$. This fraction is given by the equation:

$$\frac{dn_i}{n} = \frac{1}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{0.5} e^{-(m\dot{x}_i^2/2kT)} d\dot{x}_i. \quad (35)$$

Of special interest in chemical considerations is the fraction of the molecules which have velocities, kinetic energies, or velocity-components greater than some specified value u_0 , E_0 , or $\dot{x}_0$. This fraction of the molecules is evidently given by the integrals of the above equations between the limits u_0 , E_0 , or $\dot{x}_0$ and infinity. These integrals can be obtained (by successive integration by parts) in the form of converging series. Thus the fraction n_0/n of the molecules having kinetic energies greater than E_0 is given by the following expression, in which A is written for $E_0/(kT)$:

$$\frac{n_0}{n} = \frac{2}{\sqrt{\pi}} e^{-A} A^{0.5} \left(1 + \frac{1}{2A} - \frac{1}{(2A)^2} + \frac{3}{(2A)^3} - \dots \right). \quad (36)$$

The fraction n_0/n of the molecules having velocity-components (in one direction) greater than $\dot{x}_0$ is given by the following expression, in which B is written for $(\frac{1}{2}m\dot{x}_0^2)/(kT)$:

$$\frac{n_0}{n} = \frac{1}{2\sqrt{\pi}} e^{-B} B^{-0.5} \left(1 - \frac{1}{2B} + \frac{3}{(2B)^2} - \frac{15}{(2B)^3} + \dots \right). \quad (37)$$

Each of these expressions converges rapidly when the energy E_0 or $\frac{1}{2} m \dot{x}_0^2$ corresponding to the lower limit of the integral is much larger than kT , which is two thirds of the mean kinetic energy.

**** Prob. 26.** — *Increase with the Temperature of the Fraction of the Molecules with High Velocities in a Specified Direction.* — With the aid of Eq. 37 compute the fraction of the molecules that at 10° have values of $\frac{1}{2} m \dot{x}_0^2$ (corresponding to the velocity-component $\dot{x}_0$ in the X direction) greater than 5×409.7 k . Compare the result with that given in Table V for the same value of the energy E_0 . *Ans.* 7.2×10^{-5} .

**** Unique Velocity Values Related to the Distribution of Velocities.**

In the treatment of the kinetic theory in this book there has always been considered as the representative single velocity the *root-mean-square velocity* u (equal to $\sqrt{\Sigma u^2/n}$), which corresponds to the mean kinetic energy. This has been done because this velocity is most simply related to the temperature of fluid substances and to the pressure of perfect gases. In kinetic considerations, however, two other characteristic velocities are often em-

played; namely, the *mean velocity* $\bar{u}$ (equal to $\Sigma u_i/n$), which represents the sum of the velocities of all the molecules divided by the number of these molecules; and the *most probable velocity* u_p , defined to be the velocity which is possessed by the greatest number of molecules.

The values at any definite temperature of these two velocities (indicated by the abscissas of the lines marked $\bar{u}/u$ and u_p/u in Fig. 4) can be shown, with the aid of the expression for the distribution of velocities (Eq. 31), to be related at any specified temperature to the root-mean-square velocity u by numerical factors as follows:

$$\bar{u} = u \sqrt{\frac{8}{3\pi}} = 0.921 u; \text{ and } u_p^2 = \frac{2}{3} u^2, \text{ or } u_p = 0.8165 u. \quad (38)$$

Prob. 27. — Derivation of the Relation between Unique Values of the Velocities. — *a.* Derive from Eq. 31 the relation between the root-mean-square velocity and the most probable velocity, noting that the latter is the value of the velocity which makes dn_i/n a maximum. *b.* Derive similarly from Eq. 32 an expression for the most probable kinetic energy.

Note. — The expression also for the mean velocity can be derived from Eq. 31 by noting that each molecule in any infinitesimal group dn_i/n has substantially a velocity-ratio v , that therefore all the molecules in any such group have a sum of velocity-ratios equal to the product of v into the second member of Eq. 31, and that consequently all the n molecules in the gas have a sum of velocity-ratios equal to the integral of this product between zero and infinity (readily found by integration by parts).

**** 20. Distribution of Molecules in Fluid Systems in a Field of Force. Boltzmann's Equation.** — It has been shown (*Boltzmann, 1876*) that a new factor must be considered in case a fluid system is in a field of force (for example, in a gravitational field) such that the transfer of its molecules from one region to another (thus from one gravitational level to another) involves work, and therefore a change in the potential energy of the molecules. For, although the Maxwell distribution of velocities and kinetic energies still prevails among the molecules present in any specified region of the system, yet equilibrium considerations also require that the molecules of any particular species have in different regions concentrations which vary with the potential energies the molecules possess in those regions. Namely, representing by E_p the potential energy of a single molecule of a particular species in any region in excess of the potential energy (taken as zero) which it possesses in any reference region at the

same temperature, and representing by $\bar{n}$ and $\bar{n}_0$ the number of such molecules per unit-volume in these two regions when equilibrium prevails, this principle is expressed by the following equation, known as *Boltzmann's equation*:

$$\bar{n} = \bar{n}_0 e^{-(E_r/kT)}. \quad (39)$$

This potential-energy excess E_r is evaluated by finding expressions for the energy-content increase that occurs in the system when the (single) molecule is transferred to the specified region from the reference region. This is usually done by considering the forces, intermolecular as well as external, against which the transfer takes place.

The simplest applications of Boltzmann's equation, which alone are here considered, are those in which the system is in the state of a perfect gas; for in the case of such a system, owing to the absence of attractive forces, a molecule can be introduced or withdrawn without energy effect, so that the energy-increase attending the transfer of a molecule from one region of the system to another region is only the energy taken up in overcoming any *external* force that may exist. For example, in the case of a vertical column of a perfect gas (with molecules of mass m) in a uniform field where the force of gravity is f and the gravitational acceleration is g , the expression for the energy of transfer of one molecule from a region at the height zero to a region at the height h is $f h$ or $m g h$. This is therefore also the expression for the energy quantity E_r .

**** Derivation of Boltzmann's Equation for
Perfect Gases.**

Prob. 28.—Equilibrium in a Vertical Column of a Perfect Gas at Uniform Temperature. — *a.* Derive an expression for the ratio of the pressures p and p_0 in a column of a perfect gas at the heights h and zero from the perfect-gas laws and from the hydrostatic principle that the pressure-decrement ($-dp$) of any fluid of (variable) density $\bar{m}$ for a height-increment dh is equal to the weight (expressed as a force) of the intervening column of fluid of unit cross-section. *b.* Show that for a perfect gas this expression is identical with Boltzmann's equation $\ln(\bar{n}_0/\bar{n}) = m g h / k T$. *c.* Calculate the pressure of the atmosphere at 2000 m. above sea-level, assuming its pressure to be 1 atm. at sea-level and its temperature to be uniformly 20° , taking g as constant at 980.6, and regarding air as a single substance of molar weight 29.0.

Boltzmann's equation can be similarly derived, with the aid of semipermeable walls, for the case that several chemical species (different kinds of molecules) are present in a mixture that is in the perfect-gas state and is located in a gravitational field. Namely, one need only consider that a column of the gaseous mixture is in communication at its top and bottom, through a wall permeable only for one of the gaseous substances, with a column of that pure gas. Then, when equilibrium is established, the (partial) pressures of that substance, and in accord with Dalton's law its concentrations, will be equal at the top of the two columns, and also at the bottom; and the decrease of pressure and of concentration with the height in the column of the pure gas will evidently be given by the expressions that were found in Prob. 28.

**** Applications of Boltzmann's Equation to Gases.**

Prob. 29. — Change of the Composition of the Atmosphere with Altitude Assuming Constant Temperature, Absence of Convection, and Attainment of Equilibrium. — Owing to convection the atmosphere has up to a height of 11 km. nearly the same composition as that previously given (III, 7) for dry air at the earth's surface. At this height the pressure and temperature are normally 168 mm. and -55°C (*Humphreys, 1929, "Physics of the Air"*). Under the (arbitrary) assumptions that above this level the temperature remains constant at -55° , that there is no convection, and that the equilibrium concentrations are attained, find the molar percentages ($100x$) of oxygen, nitrogen, argon, and carbon dioxide and the total pressure p that would exist in the atmosphere at a height of 60 km. *Ans.* p , 0.0855 mm.; mol-percents: N_2 , 91.4; O_2 , 8.51; A, 0.042; CO_2 , 0.0005.

Prob. 30. — Concentration-Changes Produced in a Perfect Gas by Centrifugal Action. — A tube 80 cm. long, supported on a vertical axis midway between its ends, is rotated in a horizontal plane at the rate of 3000 revolutions per minute, in surroundings at 20° . The tube is charged with an equimolar mixture of hydrogen and oxygen. *a.* Calculate the kinetic energy due to the rotation which one molecule of each of these gases possesses at the outer ends of the tube. *b.* Calculate from Boltzmann's equation the ratio of the concentration at the ends to that at the middle of the tube for each of the gases, assuming temperature-changes and convection to be avoided so that equilibrium is established at 20° . *c.* Assuming that at the center of the tube the gaseous mixture is kept equimolar and at a total pressure of 1 atm. (for example, by passing a slow current of the mixture vertically through the tube at its axis of rotation), compute the mol-fractions of hydrogen and oxygen at the ends of the tube. *Ans.* b , H_2 , 1.0066; O_2 , 1.110.

Boltzmann's law expresses also the distribution of electrically charged molecules (ions) in an electric field; and it will be seen later that this is of much importance in the development of the ionic theory of solutions.

III. HEAT-CAPACITY OF GASES AND THE ENERGIES OF MOLECULES.

21. Experimental Determination of the Heat-Capacity of Gases. — It has already been seen (*II*, 4) that there are two important quantities related to heat-capacity represented by $\tilde{C}_p$ and $\tilde{C}_v$ and defined to be the quantities of heat dQ/dT absorbed per degree when one mol of the substance is heated at constant pressure and at constant volume, respectively. For gases in the perfect-gas state certain principles relating to these quantities have been derived (*II*, 9) from the law that the energy-content of gases in this state is independent of the pressure or volume and therefore a function only of the temperature. These principles state that both of these heat-capacities are in the case of any perfect gas independent of its pressure or volume, and that their difference is equal to the gas-constant. That is:

$$\begin{aligned}\tilde{C}_p &= f(T), \text{ and } \tilde{C}_v = f(T); \\ \text{and } \tilde{C}_p - \tilde{C}_v &= R = 1.9866 \text{ cal/degree.}\end{aligned}\tag{40}$$

The heat-capacity of gases at constant pressure can be determined by direct experiment with considerable accuracy, except at high temperatures. For this purpose there has often been employed the method previously described (*Prob.* 5; *II*, 4), in which a known weight of gas flowing per minute through a heat-insulated tube is heated through an observed temperature-interval by a measured input of electrical energy. Various other methods are also available (of which one, employing a process of adiabatic expansion, is described below).

Accurate values of the heat-capacity at constant volume, on the other hand, are difficult to obtain by direct measurement because any rigid vessel used for holding the gas has unavoidably a much larger heat-capacity than the gas itself. Heat-capacities at constant volume, which are important because they have a simpler theoretical significance than those at constant pressure, are therefore often derived from the latter by the perfect-gas equation $\tilde{C}_p - \tilde{C}_v = R$, in the case of gases at small pressures.

The *heat-capacity-ratio* C_p/C_v also can be experimentally determined by various methods. This ratio is most commonly derived from measurements of the velocity v of sound through

the gas, with the aid of the following equation, applicable to a perfect gas of molar weight M :

$$\frac{C_p}{C_v} = v^2 \frac{M}{R T}. \quad (41)$$

From the so-derived value of the heat-capacity ratio and from a measured value of $\tilde{C}_p$ the value of $\tilde{C}_v$ can obviously be calculated. Furthermore, when the value of $\tilde{C}_p$ is unknown, the values both of $\tilde{C}_p$ and $\tilde{C}_v$ can evidently be obtained from the value of their ratio C_p/C_v and of their difference $\tilde{C}_p - \tilde{C}_v$.

**** Methods of Determining Heat-Capacities.**

The above-given perfect-gas relation between the heat-capacity ratio and the velocity of sound is readily derived from the fundamental law of wave propagation, which in a medium whose wave compressions and expansions are so rapid as to be adiabatic is given by the following expression (*Laplace, 1815*):

$$v^2 = \left(\frac{\partial p}{\partial \bar{m}} \right)_{Q=0} = - \frac{\bar{v}^2}{M} \left(\frac{\partial p}{\partial \bar{v}} \right)_{Q=0}. \quad (42)$$

In this expression ∂p , $\partial \bar{m}$, and $\partial \bar{v}$ denote the changes in pressure, density, and formular volume that attend the adiabatic expansion of any fluid substance of formular weight M when the pressure increases by ∂p .

From this fundamental equation the perfect-gas relation (Eq. 41) is obtained by substituting for $(\partial p / \partial \bar{v})$ the expression for it that results by differentiating the equation $p v^{(C_p/C_v)} = \text{const.}$, which was previously derived for the reversible adiabatic expansion of a perfect gas from the equation $C_v dT = - p dv$ (Eqs. 51, 52; II, 28).

The relative values of the velocity of sound have usually been determined by measuring the relative wave-lengths in the gas and in air of the stationary sound waves produced by a tuning fork of definite pitch in a tube sprinkled with a light powder (*Kundt, Warburg, 1875*). The wave-lengths of the stationary waves (which result from superposition of the direct wave upon that reflected from the end of the tube) are found by measuring the distance between the nodes (lines of no vibration) at which the powder gathers.

However, it is to be noted that, because of large multiplication of errors in calculating the separate values of $\tilde{C}_p$ and $\tilde{C}_v$ from the experimentally derived value of their ratio and the equation $\tilde{C}_p - \tilde{C}_v = R$, the results may be seriously in error unless the velocity of sound in the gas has been very accurately determined, and unless both the formulas used (Eqs. 40, 41) are replaced by equations which take account of the deviations from the state of

perfect gas. The simplest way of eliminating errors from the latter source is, however, to determine the sound-velocity at various pressures and extrapolate to zero pressure. Error may also arise, especially in the case of gases with complex molecules, from the failure of the molecules to take up or give off in the rapid expansions and compressions the full quota of (vibrational) energy that corresponds to the heat-capacity of the gas.

Prob. 31. — Separate Values of the Two Heat-Capacities Derived from their Ratio by the Perfect-Gas Formulas. — From measurements of the relative velocities of sound in carbon dioxide and in air at 15° and 1 atm. the heat-capacity ratio for carbon dioxide at 15° and 1 atm. is found by Eq. 41 to be 1.304. *a.* Calculate the separate values of the molar heat-capacities. *b.* Calculate these values taking the heat-capacity difference equal to 2.04 cal./degree, as derived from the equation of state of carbon dioxide. *c.* Calculate these values as in *a* assuming that the observed value of the velocity of sound in carbon dioxide is 0.2 % high because of experimental error. *Ans. a,* 6.53; *b,* 6.71; *c,* 6.64.

Precise values of the heat-capacity of gases at constant pressure have recently been obtained by a method (*Lummer, Pringsheim, 1889; Eucken and others, 1929, 1932*) in which the changes in pressure and temperature attending a (sudden) adiabatic expansion of the gas are measured. The method is based on the following equation derived from the two laws of thermodynamics for the reversible adiabatic expansion of any fluid substance:

$$C_p = T \left(\frac{\partial p}{\partial T} \right)_s \left(\frac{\partial v}{\partial T} \right)_p. \quad (43)$$

In this equation, as the symbols indicate, the first partial derivative is the ratio of the changes in the pressure and temperature of the gas that attend its adiabatic expansion (at constant entropy S) from the state p, v, T to the state $p + dp, v + dv, T + dT$, and the last partial derivative denotes the change in volume of the gas with the temperature when it is heated at constant pressure. For computing the heat-capacity from an actual expansion experiment an expression for the latter derivative in terms of p and T is derived from the equation of state of the gas, and the equation is then integrated so as to obtain an expression for C_p in terms of the initial and final pressures and temperatures p_1, p_2, T_1, T_2 observed in the experiment. Thus for the state of perfect gas the resulting expression is: $\tilde{C}_p \ln (T_1/T_2) = R \ln (p_1/p_2)$.

22. Heat-Capacity of Perfect Gases in Relation to the Complexity of Their Molecules. — The heat-capacity of perfect gases is related to the complexity of their molecules, as is shown by the values given in Table VI.

TABLE VI. MOLAR HEAT-CAPACITIES AT CONSTANT VOLUME
EXTRAPOLATED TO ZERO PRESSURE.

Gas	Values of $\tilde{C}_v$ at Various Temperatures*						
	- 100°	- 30°	20°	100°	200°	400°	600° C.
He, Ne } A, Hg }	2.98	2.98	2.98	2.98	2.98	2.98	2.98
H ₂	4.18*	4.77	4.91	4.97	4.98	4.99	5.00
N ₂	4.95	4.95	4.95	4.96	5.05	5.30	—
CO	4.97	4.97	4.97	5.00	5.08	—	—
O ₂	4.98	4.99	5.04	5.15	5.38	5.85	6.19
HCl	—	—	4.98	—	—	—	—
NO	5.40	5.22	5.10	5.16	5.28	5.63	5.98
Cl ₂	—	5.80	6.03	6.31	6.62	—	—
H ₂ O	—	—	—	6.37	6.47	6.82	7.6
CO ₂	—	—	6.78	7.68	8.58	9.86	10.9
N ₂ O	—	—	7.22	7.91	—	—	—
SO ₂	—	—	7.2	—	—	—	—
NH ₃	—	6.23	6.50	7.05	—	—	—
CH ₄	—	—	6.49	7.71	9.09	—	—

* Nearly all the values between - 30° and 600°, except those for nitric oxide, water, and ammonia, are the values determined by Eucken and associates (1929, 1932) by the adiabatic expansion method described above. The values for oxygen and nitric oxide are those derived from spectroscopic data. At still lower temperature hydrogen has the following values: 3.59 at - 180°, 3.05 at - 210°, and 2.98 at - 240°.

These data lead to the following generalizations in regard to the values of the molar heat-capacity at constant volume:

(1) The gases with monatomic molecules all have the same molar heat-capacity, namely, one of 2.98, equal to $\frac{3}{2} R$, cal./degree, and this value is the same at all temperatures.

(2) Most of the gases with diatomic molecules (those with the formulas H₂, N₂, CO, O₂, HCl) (though they may show smaller values at very low temperatures) attain with rising temperature nearly the same molar heat-capacity (one between 4.9 and 5.0, equal to about $\frac{5}{2} R$, cal./degree), and this value then remains constant or increases very slowly through a range of two hundred degrees or more, after which a rather rapid increase may take place.

(3) Chlorine, though it has diatomic molecules, has a much larger value (6.0 cal./degree) even at 20°, and this value increases

rapidly with the temperature. Bromine and iodine vapors have still larger values than chlorine (thus 6.7 and 6.9 at 100°) in correspondence with the lower temperatures at which their molecules dissociate into atoms. Less dissociable diatomic gases (for example oxygen) attain large values at high temperatures.

(4) Gases whose molecules contain three to five atoms (those with the formulas H_2O , CO_2 , N_2O , SO_2 , NH_3 , CH_4) have still larger heat-capacities (6.5–7.2 for the gases at 20°); and these values increase rapidly with the temperature.

(5) Gases with still more complex molecules have much higher heat-capacities, as shown by the following values (mostly at 20°): C_2H_2 , 8.35; C_2H_4 , 8.15; C_2H_6 , 10.25; C_6H_6 , 18; $(\text{C}_2\text{H}_5)_2\text{O}$, 27.

(6) The heat-capacity of hydrogen assumes much smaller values at very low temperatures, finally attaining the value 2.98 cal/degree exhibited by gases with monatomic molecules.

23. Atomic Weights Derived from the Heat-Capacities of Gases. — The conclusion that monatomic gases have definite values (2.98 and 4.97 cal./deg.) for their molar heat-capacities at constant volume and pressure (*III*, 22), which is confirmed by theoretical considerations presented below, made it possible to determine the atomic weight of the inert elements, helium, neon, argon, krypton, and xenon, to which, because of their failure to form compounds, the method of determining atomic weights based upon Avogadro's law is not applicable.

Prob. 32. — Atomic Weight Derived from the Density and Heat-Capacity of Gases. — State what conclusion as to the atomic weight of argon can be drawn, *a*, from the fact that its density is 1.248 times that of oxygen when both are at 20° and 1 atm.; *b*, from this fact and the fact that its heat-capacity-ratio is 1.67.

Furthermore, the results derived from the heat-capacity of gases confirm the whole system of atomic-weight values derived from molecular weights determined by Avogadro's law, inasmuch as they verify the assumption that the maximum values (*III*, 3), which alone can be derived by applying that law, are the true values. Thus the heat-capacity of mercury vapor shows that its molecule consists of a single atom; and therefore its density shows that its atomic weight is 200.6, and not perhaps one half this amount, as would be the case if the smallest number of mercury atoms existing in the molecules of any investigated

gaseous substance containing mercury happened to be two, instead of one. Similarly, the molar heat-capacity of oxygen gas indicates that it contains two atoms, as was concluded from the application of Avogadro's law to it and to the volatile compounds of the element oxygen (Prob. 5; III, 3).

24. Energy-Content and Heat-Capacity of Perfect Gases in Relation to the Energies of Their Molecules. — In the previous discussion of the kinetic theory only the *translational kinetic energy* E_T of the molecules (that due to their linear motion) was considered. However, the molecules may be set in rotation as a result of their collisions, and consequently they may possess *rotational kinetic energy* E_R . The atoms within the molecules may, in addition, possess kinetic energy due to vibration, as well as potential energy arising from forces acting between the atoms and dependent upon their position with reference to one another. These constitute the *interatomic energies*, commonly called the *vibrational energy* E_v of the molecules. Hence, the energy-content of a gas may involve the molecular forms of energy shown by the following expression (as well as certain other forms of energy mentioned below which do not vary with the temperature under ordinary conditions):

$$E = E_T + E_R + E_v. \quad (44)$$

Correspondingly, the heat-capacity C_v at constant volume, equal to $(\partial E / \partial T)_v$, is given by the following expression, in which dE_T/dT has been put equal to its previously derived value $\frac{3}{2} NR$ (Eq. 15; III, 13):

$$C_v = \frac{3}{2} NR + \frac{dE_R}{dT} + \frac{dE_v}{dT}. \quad (45)$$

In accordance with modern views of atomic structure (I, 5) gases possess also *intra-atomic energy*. For example, the extranuclear electrons possess energy in relation to one another and to the nucleus; and the nuclei of atoms may have energy because of a spinning motion. These energies, however, rarely change appreciably with the temperature under ordinary conditions; and therefore it is usually not necessary to take them into account in considering heat-capacity at moderate temperatures.

The nucleus of an atom also contains a vast quantity of energy, with respect to its disintegration; but this is constant so long as the nucleus remains intact.

There are, however, exceptions to the statements that the energies of the extranuclear electrons and of the nucleus remain unchanged, even at moderate temperatures. Thus, the abnormally large molar heat-capacity of nitric oxide (NO) at low temperatures (Table VI; III, 22) is attributed to an increase within that temperature region in the energy of its extranuclear electrons. And the existence of two kinds of hydrogen gas, called parahydrogen and orthohydrogen, both with H_2 molecules and the same kind of atoms yet differing markedly in their heat-capacities at low temperatures (thus with values of $\tilde{C}_v$ at $-100^\circ C$ equal to 3.6 and 5.9 cal./deg.) is considered by the quantum theory to arise from spinning of the nuclei of the two atoms in opposite directions (in parahydrogen) and in the same direction (in orthohydrogen).

Imperfect gases possess, in addition, *intermolecular energy*, resulting from the attraction of the molecules for one another (III, 29). This energy, in case the gas is heated at constant volume, also changes only slightly, if at all, with the temperature, since in this case the distance between the molecules is not changed.

25. Theorem of Equipartition of Energy.—From classical statistical mechanics was early derived (*Maxwell, 1859; Boltzmann, 1861*) a *theorem of equipartition of energy*, which aimed to express the distribution of the total energy of a gas among the translational, rotational, and vibrational energies of its molecules. For example, according to the theorem, there is associated with each of the three rectangular components of translational motion of a molecule in a gas at temperature T the same average energy, namely, $\frac{1}{2} k T$ ergs or calories (corresponding to the fact that the molecules of a gas possess at temperature T a total translational energy of $\frac{3}{2} R T$ ergs or calories per mol (III, 13)). The equipartition theorem would also require that each molecule possess on an average $\frac{1}{2} k T$ units of rotational energy about each axis of rotation, and indeed also an equal quantity of kinetic vibrational and of potential vibrational energy corresponding to each component of vibration.

In reality, the molecules of gases do in certain cases possess the quantity of rotational energy required by the theorem, namely, around axes with respect to which the moment of inertia of the molecule is large; but, on the other hand, they may have no rotational energy around axes with respect to which this moment is very small or they may have intermediate values; *moment of inertia* I being defined as usual by the equation $I = \sum m r^2$, where m is any element of mass located a distance r from the axis of rotation. This limited applicability of the equipartition theorem has been accounted for by the theory of quantum mechanics (III, 26).

Some applications of the equipartition theorem to the heat-capacities of gases (recorded in Table VI) are here presented, and partial explanations of them are indicated.

(1) Gases with monatomic molecules, whose molar heat-capacity $\tilde{C}_v$ is $\frac{3}{2} R$ cal./deg., evidently take up only translational energy—no rotational or vibrational energy. Such gases can have, of course, no interatomic (vibrational) energy, since their molecules are identical with their atoms; and they take up no rotational energy because monatomic molecules, with their mass (disregarding the electrons) located within a single very small atomic nucleus (*I*, 5), have an extremely small moment of inertia.

(2) Gases whose molecules contain three or more atoms (not in a straight line), which have molar heat-capacities above $3 R$ units, take up, per mol per degree, $\frac{3}{2} R$ units in the form of rotational energy, and the amount in excess of $3 R$ in the form of vibrational energy; the last being larger, the more complex the molecule.

(3) Gases with diatomic molecules whose molar heat-capacity is $\frac{5}{2} R$ at room temperature take up, per mol per degree, in addition to the $\frac{3}{2} R$ units of translational energy, R units of rotational energy, but no vibrational energy. The fact that diatomic molecules have only two thirds as much rotational energy as polyatomic molecules is because diatomic molecules, with their mass located mainly in the two atomic nuclei, have a very small moment of inertia about one of the three rectangular axes, namely, about the line joining the center of the two nuclei. The same thing should evidently be true of polyatomic molecules, like those of CO_2 or C_2H_2 , whose atoms are located on a straight line.

(4) Gases with diatomic molecules whose molar heat-capacity is larger than $\frac{5}{2} R$ (as in the case of chlorine at room temperature) take up this additional energy in the form of vibration. This is in correspondence with the fact that such gases dissociate into their atoms at much lower temperatures than do those for which $\tilde{C}_v$ is $\frac{5}{2} R$. The molecules of the latter gases also acquire vibrational energy at higher temperatures, as is shown by the increase in their heat-capacity at these temperatures.

Prob. 33. — Partition of the Energies of Molecules. — From the molar heat-capacities given in Table VI (III, 22), compute and tabulate the fractions of the total energy absorbed per degree which go to increasing the translational energy, the rotational energy, and the vibrational energy of the molecules of each of the following gases at 20° and at 200° : *a*, argon; *b*, nitrogen; *c*, chlorine; *d*, carbon dioxide; *e*, methane. Assume that the rotational energy is that predicted by the equipartition theorem. Take into account the fact that the atoms of carbon dioxide lie upon a straight line.

**** 26. Rotational Energies of Molecules Interpreted by Quantum Mechanics.** — The heat-capacities of gases have recently been much more fully interpreted with respect to the types of the energies of their molecules by the recently developed science of quantum mechanics. Namely, quantum-mechanical considerations show that each particle (such as a molecule or ion) possesses (with respect to any axis of rotation) only one *quantum* of rotational energy, which consists either of a definite minimum quantity of energy or of a permissible integral multiple of that quantity; and they show that, other things equal, the magnitudes of these quanta are smaller the greater the moment of inertia of the molecules. For example, in the simple case of diatomic molecules that are rigid (that is, have no vibrational energy) the magnitudes of the rotational energy quanta are given by the following equation, in which h is Planck's constant (6.547×10^{-27} erg-sec.) and j (called the *rotational quantum number*) has any integral value 0, 1, 2, 3 ...

$$E_j = \frac{j(j+1)h^2}{8\pi^2 I}. \quad (46)$$

Furthermore, in consequence of this quantization of rotational energy, the molecules of a gas can acquire by collisions

such energy in considerable quantity (through transformation of the translational energy of other molecules) only when the temperature is such that many molecules are present which have translational energies commensurate with the respective rotational quanta. Thus, in the case of rigid diatomic molecules, many molecules must be present which have a translational energy greater than $\hbar^2/(4\pi^2 I)$ in order to raise a molecule from the zero rotational state ($j=0$) to the first rotational state ($j=1$), and greater than $3 \hbar^2/(4\pi^2 I)$ to raise it from the zero to the second rotational state ($j=2$), etc. Yet, by Maxwell's distribution law the fraction of molecules having a translational energy greater than a specified value is large only when this specified value is less than the average value $\frac{1}{2} m u^2$ (Table IV; III, 19). But, since this average value equals $\frac{3}{2} k T$ (III, 13), it follows that the molecules as a whole can acquire considerable rotational energy by collisions only when the temperature is so high that $\frac{3}{2} k T$ is larger than the smallest rotational quantum $\hbar^2/4\pi^2 I$.

It follows from these considerations that the extent to which the molecules of a gas upon heating take up rotational energy about any axis will be larger the smaller the magnitudes of the rotational quanta of the molecules, and therefore the larger their moment of inertia; also that the tendency to take up rotational energy will increase with rising temperature. Furthermore, quantum mechanics shows, as the conditions become more favorable through rise of temperature for the conversion of translational into rotational energy, that the average rotational energy of the molecules with respect to any axis approaches at any temperature T the maximum value $\frac{1}{2} k T$, which is the same as that indicated at any temperature by the theorem of equipartition of energy. Hence quantum mechanics leads to the conclusion that the actual rotational energy of the molecules about any axis may at a sufficiently low temperature, depending on their moment of inertia, be practically zero, that it will at a sufficiently high temperature become $\frac{1}{2} k T$, and that at intermediate temperatures it will have an intermediate value. And the molar heat-capacity $\tilde{C}_v$ of gases may be expected to show corresponding variations, in so far as this is dependent on this form of molecular energy.

It will be seen, without detailed discussion, that these quantum principles account for the facts: (1) that monatomic gases have a molar heat-capacity of $\frac{3}{2} R$ units, inasmuch as the mass of the molecule (disregarding the electrons) is located within the minute nucleus so that its moment of inertia must be very small and its rotational energy quanta very large; and (2) that gases with diatomic molecules have a molar heat-capacity of $\frac{5}{2} R$ units (not of $\frac{3}{2} R$ units), inasmuch as the mass is located within the two small atomic nuclei, so that its moment of inertia about the line on which the two atoms lie must be very small and the rotational quanta correspondingly large.

A striking illustration of the quantum principles is afforded by the remarkable change with the temperature of the heat-capacity of hydrogen gas (Table VI; III, 22): this behaves, it may be recalled, like a monatomic gas (with $\tilde{C}_v$ equal to 2.98 cal. at very low temperatures), but like a diatomic gas (with $\tilde{C}_v$ about 5 cal.) at room temperature, and it has intermediate heat-capacity values (affected by the existence of ortho and para hydrogen) at intervening temperatures. The diatomic molecules of this gas differ from those of other diatomic gases in the respect that its atoms have a much smaller mass (m) and are at a somewhat smaller distance ($2r$) from each other, so that its molecule has a much smaller moment of inertia ($2mr^2$) about the two axes at right angles to the line joining the atom-centers. Hydrogen therefore has a much larger value of the first rotational energy quantum $\hbar^2/(8\pi^2mr^2)$ —a value so large in fact that at temperatures below 33°A it greatly exceeds the mean translational energy $\frac{3}{2} k T$ of its molecules.

**** Prob. 34. — Quanta of Rotational Energy of Rigid Diatomic Molecules.** — Calculate the smallest quantum of rotational energy for rotation about an axis at right angles to the line joining the atom-centers, a , for oxygen gas; b , for hydrogen gas; considering (as derived from spectroscopic data) that the interatomic distances are 1.22×10^{-8} cm. in the case of oxygen, and 0.75×10^{-8} cm. in the case of hydrogen, and that the masses of the molecules are located wholly in their atom-nuclei. Calculate the values of the mean translational energy of the molecules, c , at 33°A; and d , at 293°A. Record all the results in a table, which contains also the molar heat-capacities of these gases as given in Table VI; and state the significance of the results. e, f . Calculate the temperature at which the mean translational energy of the molecules

becomes equal to the smallest rotational quantum, e , for oxygen gas, f , for hydrogen gas. g . Show that these values are in accord with the facts that the heat-capacity of hydrogen gas is at very low temperatures equal to that of monatomic gases and at room temperature equal to that of rigid diatomic gases, and that the heat-capacity of oxygen gas is, even at very low temperatures, equal to that of rigid diatomic molecules.

Ans. a, b ; E_R for oxygen, 5.52×10^{-16} ; for hydrogen, 2.3×10^{-14} .
 c, d ; mean E_T at 33°A , 6.8×10^{-15} ; at 293°A , 6.0×10^{-14} .

**** Fraction of Molecules in Each Rotational Quantum State Computed by Boltzmann's Equation.**

The foregoing considerations serve only to give a qualitative picture of the phenomena. The fraction of the molecules which possess each quantum of rotational energy (for which $j = 0, 1, 2, 3, \dots$) can be calculated by the appropriate form of Boltzmann's equation (III, 20), substituting in it the proper expression for the particular rotational energy quantum.

The specialized form of Boltzmann's equation applicable to molecules that exist in a series of quantized states j (equal to 0, 1, 2 $\dots$) is as follows:

$$\frac{n_j}{n_0} = g_j e^{-\frac{E_j}{kT}}. \quad (47)$$

In this expression E_j denotes the energy acquired by a molecule when it changes from quantum state zero to quantum state j , and n_j/n_0 is the ratio of the numbers of the molecules that exist in the j state and in the zero state. Moreover, g_j signifies the number of kinds of molecules (distinct because of different orientation of their rotational axes or of different directions of the spin of their atoms, or otherwise) which acquire the same energy E_j when they change from quantum state zero to quantum state j .

In the case of rigid diatomic molecules the expression given by Eq. 46 can be substituted for E_j ; and in the case of diatomic molecules that contain unlike atoms, such as carbon monoxide, the quantum theory shows that the quantity $2j + 1$ can be substituted for g_j , since this quantity $2j + 1$ represents the number of distinct forms in which such molecules with rotational energy E_j exist. For example, by this method, at 30°A for carbon monoxide, which is found spectroscopically to have a moment of inertia of 1.50×10^{-39} , the fractions $n_0/\bar{n}$, $n_1/\bar{n}$, $n_2/\bar{n}$, $\dots$ of the total number $\bar{n}$ of molecules which exist in the various rotational quantum states 0, 1, 2, $\dots$ are calculated to be as follows:

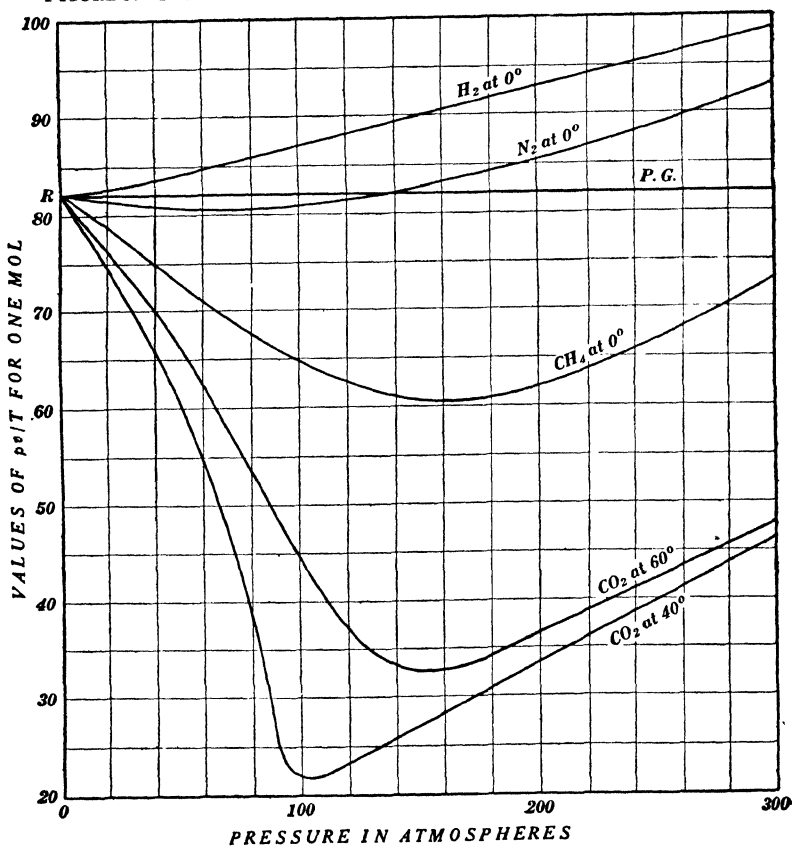
$n_0/\bar{n}$	$n_1/\bar{n}$	$n_2/\bar{n}$	$n_3/\bar{n}$	$n_4/\bar{n}$	$n_5/\bar{n}$	$n_6/\bar{n}$	$n_7/\bar{n}$
0.09	0.23	0.22	0.22	0.14	0.07	0.03	0.01

By multiplying each of these fractions by the corresponding value of E_j and summing the products (so as to give $E_1 n_1/\tilde{n} + E_2 n_2/\tilde{n} + \dots$) one finds the total rotational energy of carbon monoxide at 30° per molecule to be 4.14×10^{-15} ergs, which is equal at 30° to kT (4.12×10^{-15} ergs), in accord with the equipartition theorem.

IV. PRESSURE-VOLUME-TEMPERATURE RELATIONS OF GASES AT HIGH PRESSURES AND THEIR KINETIC INTERPRETATION.

27. Van der Waals' Equation. — The variation in the pressure-volume product at constant temperature with increasing pressure is shown for various gases by Fig. 5. As ordinates are plotted the values of $p\tilde{v}/T$ expressed in milliter-atmospheres per degree per mol, and as abscissas are plotted the values of the pressure in atmospheres. Such graphs are called *isotherms*. The straight line P. G. represents the behavior of a perfect gas, for which the product $p\tilde{v}/T$ would have a constant value R equal to 82.05 ml.-atm./deg. at all pressures and temperatures.

FIGURE 5. PRESSURE-VOLUME RELATIONS OF HIGH-PRESSURE GASES.



The departures of the graphs from the horizontal line representing a perfect gas are seen to depend in a high degree on the nature of the gas. The generalization can, however, be made that for different gases at the same temperature the deviation is less the lower the temperature of liquefaction of the gas at a pressure of one atmosphere. This relation to liquefaction-temperature is illustrated by Table VII, which supplements Fig. 5 also in the respect that it shows qualitatively the form of isotherm which various gases not represented in that figure exhibit at room temperature. The number following the chemical symbol is the absolute temperature at which under one atmosphere the gas liquefies (or in the case of carbon dioxide solidifies).

TABLE VII. ISOTHERM-FORMS AND LIQUEFACTION-TEMPERATURES OF VARIOUS GASES.

H ₂ ,	20°;	He,	4°;	Ne,	27°.	
N ₂ ,	77°;	O ₂ ,	90°;	A,	87°;	CO, 83°.
CH ₄ ,	112°.					
CO ₂ ,	195°;	C ₂ H ₄ ,	170°;	NH ₃ ,	239°.	

The pressure-volume-temperature relations of one mol of any gas are well represented up to fairly high pressures by the following equation of state, known as *van der Waals' equation*, in which a and b are constants (with respect to changes of volume, pressure, and temperature) varying with the nature of the gas:

$$\left(p + \frac{a}{\tilde{v}^2}\right)(\tilde{v} - b) = R T; \text{ or } p \tilde{v} = R T + p b - \frac{a}{\tilde{v}} + \frac{b a}{\tilde{v}^2}. \quad (48)$$

It can be shown that this reduces approximately to the moderate-pressure gas equation $p \tilde{v}(1 - \beta p) = R T$ in case one puts:

$$\beta = \frac{1}{R T} \left(b - \frac{a}{R T} \right). \quad (49)$$

Prob. 35. — Application of High-Pressure Isotherms. — Determine from Fig. 5 the number of kilograms of CO₂ that can safely be charged into a 15-liter steel tank which will withstand a pressure, a , of 50 atm.; b , of 100 atm.; c , of 150 atm. Assume that the tank might be exposed (under a summer sun) to a temperature as high as 40°.

Prob. 36. — Discussion of Van der Waals' Equation. — a. Explain how the differing initial slopes of the graphs of hydrogen and of methane can be accounted for by appropriate values of b and $a/\tilde{v}^2$. *b.* Derive Eq. 49, noting that, though at moderate

pressures $a/\tilde{v}^2$ and b are not negligible in comparison with p and $\tilde{v}$ respectively, yet in the terms containing these small quantities certain approximations can be made.

28. Derivation of Van der Waals' Constants and Their Experimental Testing. — The constants of van der Waals' equation can be most simply derived and an estimate of the accuracy of the equation obtained by applying it to measurements of the pressures shown in the same volume of any definite gas at different temperatures.

This will be clear from the following considerations. By solving van der Waals' equation for the pressure there is obtained:

$$p = \frac{R}{\tilde{v} - b} T - \frac{a}{\tilde{v}^2}. \quad (50)$$

By putting $R/(\tilde{v} - b) = B_v$ and $a/\tilde{v}^2 = A_v$, where B_v and A_v are functions which should depend only on the molar volume $\tilde{v}$ of the gas under consideration and on its constant b or its constant a , it is seen that the pressure p_v at constant volume should be a linear function of the absolute temperature T , as expressed by the equation $p_v = B_v T - A_v$. Any form of graph for which v is constant is called an *isochore*. By substituting in this equation pressures observed at two different temperatures at any definite molar volume, values of B_v and A_v may be obtained, and from these there may be calculated values of van der Waals' constants b and a . Best representative values of these constants for a wide range of conditions may then be found by computing a series of values for different pairs of temperatures and for different molar volumes, and adopting a weighted mean value for each constant.

Tests of the validity of van der Waals' equation are afforded, first, by the approximation with which at constant volume the pressure p_v is a linear function of the temperature T , and secondly, by the agreement of the b and a values computed for different molar volumes. A better judgment of the adequacy of the equation, however, can be formed by the converse procedure; namely, by comparing observed values of $p\tilde{v}$ at widely different pressures and temperatures with the values computed by the equation with the aid of the best representative values of the constants b and a derived as in the preceding paragraph.

Prob. 37. — Experimental Determination of Van der Waals'

Constants. — *a.* Derive from the following experimental data (*Keyes, Burks, 1927*) for methane CH_4 four equations of the form $p_v = B_v T - A_v$ (using 100° temperature ranges) and four values of the constant b and of the constant a :

Molar volume (ml.)	640	640	640	320	320	320
Temperature ($^\circ\text{C}$)	0	100	200	0	100	200
Pressure (atm.)	32.297	46.474	60.486	60.13	91.24	121.81

b. Tabulate these values of b and a ; also means of each four values.

Ans. { Values of b : 61.2, 54.4, 56.3, 51.6; mean, 55.9.
 { Values of $a \times 10^{-6}$: 2.63, 2.38, 2.54, 2.34; mean, 2.47.

Prob. 38. — Experimental Tests of Van der Waals' Equation.

— With the aid of the mean values of the constants obtained in Prob. 37 calculate the value of $p\tilde{v}$ for methane, at $t = 0^\circ$, $\tilde{v} = 640$ ml.; at $t = 200^\circ$, $\tilde{v} = 320$ ml.; and at $t = 100^\circ$, $\tilde{v} = 240$ ml. Tabulate these calculated values beside the observed values of $p\tilde{v}$ calculated from the pressures given in Prob. 37 and from the observed pressure at $t = 100^\circ$ and $\tilde{v} = 240$ ml., which is 120.85 atm. Tabulate also the percentage difference between each calculated and observed value. (Note that the use of the mean values of b and a would for mathematical reasons necessarily result in close agreement between the calculated and observed $p\tilde{v}$ values only at $t = 100^\circ$ and $\tilde{v} = 480$.)

Table VIII shows the degree of agreement of the $p\tilde{v}$ values calculated by van der Waals' equation at various temperatures and molar volumes with the observed $p\tilde{v}$ values for methane (*Keyes, Burks, 1927*) and carbon dioxide (*Amagat, 1893*; for a summary see *Beattie, Bridgeman, 1928*). These are two gases which at room temperature deviate from the perfect-gas law to a fairly large and to a very large extent, respectively. The values of the constants b and a that were used are those given above the table; they were derived in the way described above at the molar volume 400 ml. for the full temperature-interval given in the table. All pressures are expressed in atmospheres, and all volumes in milliliters. The value 82.05 was used for the gas-constant (Table II; *I, 14*), and the value 273.16 for the absolute temperature corresponding to 0°C (*I, 11*). The percentage differences given are 100 times the values of $p\tilde{v}$ (calc.) — $p\tilde{v}$ (obs.) divided by $p\tilde{v}$ (obs.). Such calculated values as correspond to the data from which the constants b and a were derived are enclosed within parentheses. The last two columns of the table

show the ratio of the volume-correction b to the observed volume v , and the ratio of the pressure correction $a/\tilde{v}^2$ to the observed pressure p . The kinetic significance of these quantities is considered below.

TABLE VIII. OBSERVED VALUES AND VAN DER WAALS' VALUES OF THE PRESSURE-VOLUME PRODUCT.

Methane, CH_4 ; $b = 56.1$, $a = 2.504 \times 10^6$.

Carbon dioxide, CO_2 ; $b = 98.6$, $a = 5.96 \times 10^6$.

	Molar Volume	Pressure	Temp. ° C.	Pressure-Volume Product			$\frac{b}{\tilde{v}}$	$\frac{a/\tilde{v}^2}{p}$
				Calculated	Observed	% Diff.		
Methane	22 364	1.00	0	22 356	22 364	-0.04	0.002	0.005
	666.7	31.16	0	20 720	20 770	-0.24	0.084	0.181
		58.18	200	38 640	38 790	-0.39		0.097
	400	49.52	0	(19 810)	19 810	(± 0.0)	0.140	0.316
		97.25	200	(38 900)	38 900	(± 0.0)		0.161
	250	74.40	0	18 880	18 600	+1.5	0.224	0.538
		157.44	200	40 050	39 360	+1.7		0.254
	200	89.75	0	18 620	17 950	+3.7	0.280	0.700
		199.35	200	41 420	39 870	+3.9		0.314
Carbon Dioxide	22 258	1.00	0	22 246	22 258	-0.05	0.004	0.012
	2000	11.26	20	22 320	22 520	-0.9	0.049	0.132
	666.7	29.43	20	19 270	19 620	-1.8	0.148	0.456
		35.42	60	23 130	23 610	-2.0		0.379
		41.32	100	26 970	27 550	-2.1		0.325
	400	42.55	20	(17 020)	17 020	(± 0.0)	0.246	0.876
		53.65	60	21 370	21 460	-0.4		0.695
		64.32	100	(25 730)	25 730	(± 0.0)		0.579
	250	54.56	20	15 860	13 640	+16.	0.394	1.75
		74.68	60	21 280	18 670	+14.		1.28
		93.72	100	26 700	23 430	+14.		1.02
	200	65.45	30	19 240	13 090	+47.	0.493	2.28
		85.35	60	24 100	17 070	+41.		1.75
		110.70	100	30 580	22 140	+38.		1.35

Table VIII shows that both for methane and for carbon dioxide there exist values of the constants b and a which enable an equation of van der Waals' form to express the pressure-volume-temperature relations of gases with a small percentage error (one of less than 2%), so long as the molar volume is not too small (thus not less than 250 ml. for methane, or 400 ml. for carbon dioxide). For these substances at any rate, this is true for a considerable variation of temperature (0 to 200° or 0 to 100°), of pressure (0 to 160 or 0 to 65 atm.), and of molar volume (22 000 to 250 or to 400 ml.).*

At molar volumes much smaller than 250 to 400 ml. van der Waals' equation may give very erroneous values of the pressure-volume if the constants b and a used are derived at moderate pressures. This is especially true if an equation with so-derived constants be applied to the computation of the values of the molar volume at or near the critical temperature and pressure. Correspondingly, very divergent values of the constants b and a are obtained when these constants are computed, as is often done, with the aid of certain expressions for them which can be derived by applying van der Waals' equation to the critical temperature, pressure, and volume of substances. Thus for carbon dioxide there have been derived from critical data the value 42.8 for b and the value 3.61 for $10^{-6} a$, instead of those (98.6 and 5.96) given in Table VIII. Values of the constants so derived from critical data should, of course, not be employed in applications involving pressures that are only moderately high.

At very high pressures agreement with observed values can be attained by introducing into van der Waals' equation additional constants characteristic of the substance, or by formulating new equations of state; and a very large number of such equations of state have in fact been proposed. An example of an equation of this kind, one which has been shown to hold through a wide range of pressure and temperature, is the following,

* It is noteworthy that also the accurately measured values at one atmosphere and 0° (given in the first row of each section of the table) are fairly concordant with those calculated from the constants b and a derived from the data at much higher pressures and temperatures. This is better shown by the agreement of the observed deviation-coefficient 100β (Eq. 5; III, 4) with that calculated from the constants derived from the higher-pressure measurements (Eq. 49; III, 27); thus the values of these quantities at 0° and 1 atm. are: for methane, -0.22 obs., -0.25 calc.; for carbon dioxide, -0.70 obs., -0.75 calc.

which supplements van der Waals' constants b and a by two other constants l and α characteristic of the substance:

$$\left(p + \frac{a}{(\tilde{v} - l)^2}\right)(\tilde{v} - be^{-\alpha\tilde{v}}) = RT \quad (\text{Keyes, 1917}).$$

Another equation of state, which has been much used for empirical purposes, is the following one, in which the pressure correction is made inversely proportional to the absolute temperature:

$$\left(p + \frac{a}{T\tilde{v}^2}\right)(\tilde{v} - b) = RT \quad (\text{D. Berthelot, 1903}).$$

The equations of state of gases at very high pressures, as well as the principles regarding the continuity of the gaseous and liquid states to which these lead and their relations to the critical constants of substances, constitute an important and extensive division of physical chemistry. These topics are not considered in this book, however; for the treatment is complicated, and the results are significant from a physical, rather than from a chemical standpoint—a fact sometimes recognized by considering the topics to belong to “chemical physics,” instead of to physical chemistry. Moreover, they have not yet led to very definite kinetic molecular principles.

29. Kinetic Derivation of Van der Waals' Equation. —

As the pressure of a gas increases, two effects that were neglected in the derivation of the kinetic equation for perfect gases (*III, 10*) must be taken into account; namely, the effect of the volume occupied by the molecules themselves, and the effect of any force of attraction between the molecules. These influences affect the two factors whose product is equal to the pressure of the gas—the number of impacts on the unit-surface in unit-time, and the change of momentum attending each impact.

That the number of impacts upon unit-surface of the wall in unit-time is increased in case the molecules have an appreciable volume becomes evident when it is considered that collisions with other molecules result in a shortening of the distance to be traversed by the molecules between the walls of the container. This shortening of path depends on the size of the molecules and on the character of the collision, varying from the

diameter d of the molecule when the collision is head-on to zero when it is tangential, as is seen by reference to Fig. 2 (III, 16). A rigorous mathematical analysis shows that the distance between the walls of the container to be traversed by the molecules is in effect diminished, and therefore that the number of impacts per second is increased, in the ratio $\tilde{v}/(\tilde{v} - 4\tilde{n}v_m)$, where $\tilde{v}$ is the molar volume of a pure gas consisting of $\tilde{n}$ molecules, each of which has a volume v_m . As usual in gas-kinetic considerations, the molecules are assumed spherical, so that the volume v_m of a single molecule is equal to $\frac{1}{6}\pi d^3$, where d is its diameter, interpreted as previously described. Representing by b as before (Eq. 27; III, 16) the effective volume $4\tilde{n}v_m$ of the $\tilde{n}$ molecules in one mol of the gas under consideration, the resulting increase in the number of impacts upon the wall and in the pressure p of the gas may be taken account of by writing the kinetic equation (Eq. 12; III, 10) in the form $p(\tilde{v} - b) = \frac{1}{3}\tilde{n}mu^2$.

To show the effect of the attraction of the molecules, it may be recalled that the pressure of a gas is equal to the sum of the changes in the component of momentum perpendicular to the wall experienced by all the molecules which impinge on unit-surface in unit-time; and for simplicity it may be assumed, as in the approximate derivation of the perfect-gas kinetic equation (Prob. 17; III, 10), that all the molecules of the gas are moving with uniform velocity in directions at right angles to the walls of a cubic container. However, account will now be taken of the fact that during the time that any molecule approaching the wall traverses the adjacent layer of the gas such a molecule is subjected to an inward-directed force arising from the unbalanced attraction of the gas molecules behind it.

In consequence of this inward attraction, the momentum with which a molecule reaches the wall is reduced from its normal value by an amount proportional to the attractive force acting and to the time during which it acts. For any definite gas this attractive force is evidently proportional to the number $\tilde{n}/\tilde{v}$ of the (attracting) molecules in unit-volume. Furthermore, the time during which this force acts is that required for the molecule to traverse the adjacent layer of the gas. This time, however, is inversely proportional to the quantity $u\tilde{v}/(\tilde{v} - b)$, which is greater than the velocity u , because of the above-considered

shortening of path of the molecules. Hence, introducing a proportionality-constant a' characteristic of the gas, a molecule at the instant when it strikes the wall (at right angles to it) will have a momentum less than the perfect-gas value $m u$ by the product of the force acting and the time during which it acts, namely by $a'(\tilde{n}/\tilde{v})(\tilde{v}-b)/(\tilde{v}u)$. And the change of momentum of all the molecules striking unit-surface per unit-time, which is equal to the pressure p of the gas, will obviously be found by multiplying twice this quantity by the expression for the number of impacts per unit-surface per unit-time. This is readily seen to be $\frac{1}{6} \tilde{n} u/(\tilde{v}-b)$, when it is assumed that all the molecules are moving with uniform velocity and in directions normal to the walls of the container.

These effects of the volume and of the attraction of the molecules may, under the simplifying assumptions made, be summarized as follows:

	Perfect Gas	Imperfect Gas
Impacts per sqcm. per second	$\frac{\tilde{n} u}{6 \tilde{v}}$	$\frac{\tilde{n} u}{6(\tilde{v}-b)}$
Change of momentum per impact	$2 m u$	$2 \left(m u - \frac{a' \tilde{n}}{\tilde{v}} \frac{\tilde{v}-b}{u \tilde{v}} \right)$
Pressure p	$\frac{\tilde{n} m u^2}{3 \tilde{v}}$	$\frac{\tilde{n} m u^2}{3(\tilde{v}-b)} - \frac{a' \tilde{n}^2}{3 \tilde{v}^2}$

Replacing $\frac{1}{3} a' \tilde{n}^2$ by a single constant a the foregoing result may be written in the following form, which may be called *van der Waals' kinetic equation*:

$$\left(p + \frac{a}{\tilde{v}^2} \right) (\tilde{v}-b) = \frac{1}{3} \tilde{n} m u^2. \quad (51)$$

Though this equation was here obtained with the aid of certain simplifying assumptions, yet, as in the case of the perfect-gas equation (III, 10), a rigorous treatment leads to the same result.

Since for any fluid substance $\frac{1}{3} \tilde{n} m u^2 = R T$ (Eq. 15; III, 13), van der Waals' equation of state (Eq. 48; III, 27) is an immediate consequence of this kinetic equation. Moreover, the derivation of the latter shows that the experimentally determined constant b in the empirical equation of state represents, at least approximately, four times the volume of the molecules in one

mol of gas. The derivation shows also that the externally measured pressure p is the resultant of an outward-directed pressure, represented by $RT/(\tilde{v}-b)$, caused by the motion of the molecules, and of an inward-directed pressure, represented by the term $a/\tilde{v}^2$, caused by their mutual attraction. The former of these two component pressures is often called the *thermal pressure*, since it is the pressure that within the gas would result from the translational motion of the molecules, which also determines its temperature; and the latter is usually called the *cohesion-pressure* or *attraction pressure* p_A .

The magnitudes of these quantities are illustrated by the last two columns of Table VIII, which contain ratios of the effective volume b of the molecules to the molar volume $\tilde{v}$ of the gas and ratios of the cohesion-pressure $a/\tilde{v}^2$ to the pressure p of the gas, in the case of methane and carbon dioxide at various molar volumes and temperatures.

Divergences from van der Waals' equation at small molar volumes may arise not only from the fact that the volume and attraction corrections become inaccurate for physical reasons, but also from the fact that changes in the molecular state of the gas may take place. Such changes in molecular state may result from the *aggregation* or *clustering* of molecules in consequence of van der Waals' attraction or other physical forces (as in the formation of H_4O_2 , H_6O_3 , etc., out of H_2O), or from the formation of a new molecule species through chemical *association* (as of N_2O_4 from NO_2). Vapors or liquids that give no evidence of such molecular aggregation or association are called *normal* vapors or liquids.

Prob. 39. — Relative Values of the Three Pressures. — Find the ratio of the cohesion-pressure and of the observed pressure for carbon dioxide to the thermal pressure, a , at 0° and 1 atm.; b , at 20° and 42.55 atm.

30. Molecular Magnitudes Derived from Van der Waals' Equation. Molecular Diameters Compared with Those from Viscosity-Coefficients. — From observed data (summarized by *Beattie, Bridgeman, 1928*) the values of van der Waals' constant b (in ml.) and constant a (in atm.-ml.²) for several gases have been derived through their isochores, mostly at a molar volume of 400 ml., at temperatures of 0° and 100° (20° and 100° for carbon

dioxide) in the way previously described (*III*, 28). These values are given in the second and third columns of Table IX. In an adjoining column are given the absolute temperatures at which the gas liquefies at one atmosphere. The next column of the table contains the values of the diameter d of the molecules calculated from these values of their effective volume b by the equation $b = \frac{2}{3} \pi \tilde{n} d^3$; and an adjoining column contains the values of the same quantity d calculated from the viscosity-coefficient η of the gas at 0°C by the equation $d^2 = 2.70 \times 10^{-21} \sqrt{M T}/\eta$ (Eqs. 25, 26; *III*, 16); these last values of d consisting for the most part of those recorded in Table III (*III*, 18). The attraction-constant a also can be determined by an independent method involving a different principle (*III*, 32); and this gives results (see Table X) fairly concordant with those given in Table IX.

TABLE IX. VAN DER WAALS' CONSTANTS AND RELATED MAGNITUDES.

Gas	Constant		Liquefaction Temperature	Molecule-Diameter in 10^{-8} cm. from	
	b	$10^{-6} a$		Van der Waals' b	Viscosity at 0°
He	9.4	0.00	4°A	1.95	2.18
H ₂	19.6	0.133	20	2.49	2.72
Ne	16.8	0.139	27	2.36	2.59
A	40.0	1.40	87	3.16	3.66
O ₂	41.5	1.46	90	3.20	3.64
CH ₄	59.0	2.59	112	3.59	4.15
CO ₂	98.6	5.96	195	4.26	4.62
NH ₃	195.	11.8	240	5.35	4.48

The values for ammonia gas were derived from data for its pressures at a molar volume of 1005 ml. at 60.31° and 119.34°C (*Keyes*, 1921; *I.C.T.*, 3, 11); for helium from its pressures at 1800 ml. at 0° and 100° (*Keesom, van Santen*, 1933).

The results of Table IX lead to the following conclusions:

(1) The effective volume b of monatomic molecules is larger, the greater the number of their extranuclear electrons (*I*, 5); and that of other molecules is larger, the greater the number and size of their atoms.

(2) The attraction between the molecules expressed by the constant a also increases with the complexity of the molecules; but more marked is the parallelism between its value and that of the temperature of liquefaction of the gas at one atmosphere

— a parallelism connected with the fact that it is primarily the attraction of its molecules that causes a gaseous substance to assume the liquid state.

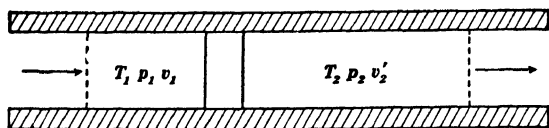
(3) The diameters of the molecules derived from van der Waals' constant b are of about the same magnitude as those derived from the viscosity-coefficient η , which is theoretically related to the cross-section $\frac{1}{4} \pi d^2$ of the molecules (Eqs. 25, 26; III, 16). This confirms the underlying kinetic considerations, and again shows that molecules with a small number of atoms have a diameter of 2 to 4 angstroms (2 to 4×10^{-8} cm.). Indeed, except in the case of ammonia, the diameters derived from the two properties differ by a nearly constant factor of 12%, indicating a corresponding minor error in one or other of the two kinetic expressions.

V. HEAT-CONTENT AND ENERGY-CONTENT OF IMPERFECT GASES.

**** 31. Determination of the Increase in Heat-Content and Energy-Content of Imperfect Gases.**—Actual gases show deviations from the energy-content law of perfect gases (*II*, 9), which states that at any definite temperature the energy-content or heat-content of the gas is independent of its volume and pressure. These deviations lie in the direction that the energy-content of the gas increases with decrease in its pressure. They are small at atmospheric pressure, increase rapidly with the pressure, and usually become large at 30–100 atmospheres.

The increase in heat-content attending isothermal expansion of a gas has usually been experimentally determined by *porous-plug experiments* (*Joule, Thomson, 1854*), in which the gas is caused to flow continuously through a well-insulated tube containing a plug of porous material, as illustrated in Fig. 6. For example, a current of gas at pressure p_1 , volume v_1 , and temperature T_1 is passed steadily through a hardwood tube containing a porous plug of cotton, whereby its pressure falls to p_2 and its volume increases to v_2' ; and at this pressure it emerges from the tube into the atmosphere. After the gas has flowed so long that every part of the apparatus has assumed the temperature of the gas in contact with it, the issuing gas is found to be at T_2 .

FIGURE 6. POROUS-PLUG APPARATUS.



Under these conditions the gas expands without taking up heat from the surroundings and without producing work other than that equivalent to the change in its pressure-volume product, hence without change in its heat-content. The decrease in temperature which the gas undergoes divided by its decrease in pressure is called the *Joule-Thomson coefficient*. By multiplying this accurately measured decrease in temperature by the heat-capacity of the gas $\tilde{C}_{p_2}$ at the constant pressure p_2 (assuming this heat-capacity can be considered independent of the temperature) the increase in the heat-content that would have attended an

isothermal expansion of the gas from the same initial pressure to the same final pressure is calculated. By subtracting from this the increase in the pressure-volume product, the increase in the energy-content is also obtained. That is:

$$\Delta \tilde{H} = (T_1 - T_2) \tilde{C}_{p_2}. \quad (52)$$

$$\Delta \tilde{E} = \Delta \tilde{H} - (p_2 \tilde{v}_2 - p_1 \tilde{v}_1).$$

**** Prob. 40. — Change in Heat-Content and Energy-Content Determined by Porous-Plug Experiments.** — *a.* State what other process must be combined with the adiabatic expansion of the gas described above in order that the net result of the two processes may be the isothermal expansion of the gas from pressure p_1 to pressure p_2 at a temperature T_1 , considering one mol of the gas. *b.* Formulate expressions (Prob. 8, Note; II, 6) for the work produced W , the heat absorbed Q , the heat-content increase $H_2 - H_1$, and the energy-content increase $E_2 - E_1$, for each of these two processes. (Note that in the first process a volume $\tilde{v}_1$ of the gas disappears on one side of the plug under a constant pressure p_1 , and that a volume $\tilde{v}_2'$ of the gas is produced on the other side of the plug under a constant pressure p_2 ; and consider that in the second process the final volume becomes $\tilde{v}_2$.) *c.* Combine the results of the two processes so as to give expressions for the increase in heat-content $\Delta \tilde{H}$ and in energy-content $\Delta \tilde{E}$ that attend at a constant temperature T_1 a change in the pressure of one mol of the gas first from p_1 to p_2 , and then per atmosphere of pressure. *d.* Calculate in calories the change in heat-content and in energy-content attending the expansion of 1 mol of carbon dioxide (1 CO_2) from a pressure of 3 atm. to a pressure of 1 atm. at 20° , using the following data: From a series of experiments with carbon dioxide (Joule, Thomson, 1862), corrected to correspond to the conditions $p_1 = 3$ atm., $p_2 = 1$ atm., $T_1 = 20.00^\circ$, it was found that T_2 was 17.72° . The molar volume of carbon dioxide at 20° and 3 atm. is 7878 ml., and at 20° and 1 atm. it is 23 920 ml.; its molar heat-capacity at 20° and at a constant pressure of 1 atm. is 8.86 cal./deg. *e.* For comparison, calculate the work in calories that would be produced in the surroundings if the expansion described in *d* took place at 20° against an opposing pressure kept substantially equal to that of the carbon dioxide, regarding it in this calculation as a perfect gas. *Ans.* *d.* $\Delta \tilde{H}$, 20.2 cal.; $\Delta \tilde{E}$, 13.3 cal.; *e.* 640 cal.

**** Prob. 41. — Analytic Derivation of the Relation between the Temperature-Drop Attending an Adiabatic Expansion and the Heat-Content Increase Attending the Corresponding Isothermal Expansion.** — Derive a relation between $(\partial T / \partial p)_E$ and $(\partial H / \partial p)_T$.

for the case named in the title from the general heat-content equation (Eq. 21; *II*, 6). Show that the so-obtained expression becomes identical with that obtained in Prob. 40c when (small) finite increments are substituted for the infinitesimal increments.

The increase in heat-content attending isothermal expansion has also been recently determined by a calorimetric method, apparently with great accuracy (*Keyes, Collins, 1932; Washburn, Rossini, Frandsen, 1932*). This method differs from a Joule-Thomson experiment in that the flowing gas, instead of cooling off as a result of the increase in its energy-content, is kept at constant temperature by a (measured) input of electric energy. For example, when ammonia gas at 27.1°C and 2.40 atm. flowed through a capillary within a calorimeter and issued at a pressure of 1.00 atm., it was found that 34.7 cal. of energy had to be imparted to each mol of the gas, in order that it might emerge without change of temperature. By dividing this energy-input by the pressure-decrease (1.40 atm.) there is directly obtained the increase in molar heat-content per atmosphere at 27.1°.

32. Energy-Content of Imperfect Gases in Relation to Cohesion-Pressure and Van der Waals' Attraction-Constant. — The energy-content increase that attends the isothermal expansion of an imperfect gas may be considered from a kinetic viewpoint to result from displacement of its cohesion-pressure p_A through the increase in volume that occurs, or from the viewpoint of the van der Waals' equation to correspond to the overcoming of the molecular attraction represented by the attraction-constant a . The molar energy-content increase is therefore expressed by the following equations:

$$d\tilde{E} = p_A d\tilde{v} = \frac{a}{\tilde{v}^2} d\tilde{v}; \quad (53)$$

$$\Delta\tilde{E} = \int_{\tilde{v}_1}^{\tilde{v}_2} p_A d\tilde{v} = a \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}_2} \right). \quad (54)$$

**** Prob. 42. — Energy-Content Increase Evaluated from Van der Waals' Attraction-Constant.** — Calculate the energy-content increase in calories that attends the isothermal expansion of 1 CO₂ from 3 atm. to 1 atm. at 20° from the value (5.96×10^6) of the attraction-constant for carbon dioxide and the molar volumes given in Prob. 40d; and tabulate this value beside that there derived from the porous-plug experiment. *Ans.* 12.3 cal.

Table X illustrates the degree of conformity of the values of the attraction-constant a for various gases, obtained on the one hand as previously described from p - v - T data by using the isochore form of van der Waals' equation (Eq. 50, and Table VIII; III, 28); and obtained on the other hand from energy-content-increase data by using van der Waals' energy-content equation (Eq. 54). The values of a are expressed in atm.-ml.² and are multiplied by 10^{-6} . The values given for the molar energy-content increase $\Delta\tilde{E}$ were obtained by subtracting $\Delta(pv)$ from the molar heat-content increase $\Delta\tilde{H}$ experimentally determined by the method indicated by the foot-notes.

TABLE X. COHESION-CONSTANTS DERIVED FROM PRESSURE-VOLUME-TEMPERATURE DATA AND FROM ENERGY-CONTENT-INCREASE MEASUREMENTS.

Gas	Temperature (°C)	Pressure (in atm.)		Volume (in ml.)		Observed $\Delta\tilde{H}$ (in cal.)	Corresp. $\Delta\tilde{E}$ (in cal.)	Constant $10^{-6}a$	
		Initial	Final	Initial	Final			by Eq. 50	by Eq. 54
O ₂	28	15.55	1.00	1575	24 592	27.4	22.6*	1.46	1.57
CO ₂	27.1	3.92	1.00	6155	24 503	27.65†	18.60	5.96	6.32
NH ₃	27.1	2.40	1.00	9926	24 150	33.70†	25.8	11.8	18.0
He	20	13.49	6.33	1794	3 812	-2.18‡	-0.26	0.00	-0.04

* By calorimetric method (Washburn, Rossini, Frandsen, 1932).

† By calorimetric method (Keyes, Collins, 1932).

‡ From Joule-Thomson coefficient (Roebuck, Ostenberg, 1933), heat-capacity (Scheel, Heuse, 1913), and p v isotherms (Keesom, van Santen, 1933).

The fair agreement of the values calculated from the heat-content change with those derived from p - v - T data shows that the term $a/\tilde{v}^2$ in van der Waals' equation of state does in reality represent the cohesion-pressure. This agreement again confirms the conclusion that this equation is a fairly satisfactory expression of related properties down to a molar volume of 400 ml. Noteworthy are the results with helium, whose isotherms, down to a molar volume of 2000 ml., show no evidence of an $a/\tilde{v}^2$ term, that is, of molecule attraction, and whose energy-content increase on expansion leads correspondingly to an extremely small value of $10^{-6}a$ (indeed to a negative one).

CHAPTER IV

THE PROPERTIES OF SOLUTIONS AND THE MOLECULAR THEORY

I. SOLUTIONS IN GENERAL.

1. **Expressions for the Composition of Solutions.**—A solution is a physically homogeneous mixture of two or more substances. Or, from a molecular view-point, a solution is a mixture of substances which has no larger aggregates than the molecules themselves. Solutions thus defined may be gaseous, liquid, or solid; but liquid solutions are mainly considered in this chapter. When one substance is present in large proportion, this substance is called the *solvent*, and any other substance present in small proportion is called a *solute*; but this is evidently a purely conventional distinction. In considering the equilibrium of solutions with their vapor or with a solid substance, the terms phase and component (*I*, 16) are often employed.

With reference to the proportions in which substances are present, two groups of solutions may be distinguished: *dilute* solutions, those in which the mol fraction of the solute is small (not greater than about 0.02); and *concentrated solutions*, those in which each substance is present in considerable proportion. There is, of course, no sharp line of demarcation between these two groups of solutions.

To express the composition of solutions the relative quantities of solute and solvent must be specified in some way. The quantity of solute present may be shown by specifying its weight m , or its number of formula-weights N^F , of equivalents N^{Eq} or of mols N (*I*, 9), the last being understood to correspond to the molecular weight M of the chemical species that exists as solute in the solution. The quantity of solvent present may be shown by specifying its weight m_0 , or the number of formula-weights N_0^F or mols N_0 corresponding to the molecular weight M_0 of the solvent in the state of vapor (*I*, 8); or there may be specified the volume v_0 occupied in the pure liquid state by the quantity of solvent present in the solution (properties of the pure solvent being denoted by letters with the subscript zero). Fi-

nally there may be specified the (total) volume v of the solution (of solute and solvent together).

By combining any one of these expressions for the quantity of solute with any one of those for the quantity of solvent or with that for the volume of the solution an expression for the composition of the solution may be obtained. Of the many possible combinations those commonly employed in this book are summarized in Table I, so that they may be available for future reference. The definitions are given in terms of the symbols used in the preceding paragraph. The quantity named (such as the mol-fraction or volume-molality) is always understood to refer to the solute, unless the word solvent is prefixed to the name (as in the expression solvent-mol-fraction X_0).

TABLE I. EXPRESSIONS FOR THE COMPOSITION OF SOLUTIONS AND CONCENTRATION OF SOLUTES.

Name	Abbreviation	Symbol	Definition
Weight-percentage	%	%	$\frac{100 m}{m_0 + m}$
Mol-fraction	—	X	$\frac{N}{N_0 + N}$
Weight-molality	wm.	c	$\frac{m_0 \text{ (in kg.)}}{N^F}$
Weight-formality	wf.	c	$\frac{m_0 \text{ (in kg.)}}{N^{Fq}}$
Weight-normality	wn.	c	$\frac{m_0 \text{ (in kg.)}}{N}$
Volume-molality	vm.	c_v	$\frac{v \text{ (in l.)}}{N^F}$
Volume-formality	vf.	c	$\frac{v \text{ (in l.)}}{N^{Fq}}$
Volume-normality	vn.	c_v	$\frac{v \text{ (in l.)}}{N^{Eq}}$
Volume-normality (in ml.)	$\overline{vn.}$	$\overline{c}_v$	$\frac{v \text{ (in ml.)}}{N^{Eq}}$

All the quantities in the last seven rows of the table are expressions of *concentration*; and the terms molal concentration, formal concentration, and normal concentration are often used

in place of the words molality, formality, and normality. Volume-concentrations are sometimes referred also to the volume of solvent associated with the quantity of solute, instead of to the total volume of the solution: these concentrations may be specified to be so referred, or they may be indicated* by the subscript v_0 , for example, c_{v_0} .

The words *molal* and *formal* (like *normal*) here denote concentrations, whereas the words *molar* and *formular* denote any property that is referred to a certain weight of substance, namely, to one mol or one formula-weight, as in the expressions molar heat-capacity and formular volume.

The terms *molal* and *formal* denoting concentration have, of course, a difference in significance corresponding to that between the terms *mol* and *formula-weight* (*I*, §). Thus the term *formal*, like the term *normal*, refers to the solute as a component, that is, to the quantity of it actually taken in making up the solution; but the term *molal*, though used by many authors to include the idea here denoted by *formal*, is in this book employed to denote the concentration of some definite chemical species, that is, of a substance consisting of some particular kind of molecules.

The composition or concentration of a solution that is expressed in terms of weight-quantities alone (thus in any of the ways shown in the upper part of the table) does not vary with the temperature. On this account this method of expression is advantageously employed in thermodynamic considerations and mass-action formulations. Volume composition or concentration,

* Subscripts and superscripts are used systematically in this book as follows:

Italic capitals and italic small letters are used as subscripts to show constant factors determining the quantity to which they are attached, like C_p .

Roman small capitals are used either as subscripts or superscripts (when double subscripts cause confusion) to show the type of the general property denoted by the main symbol that is under consideration, like Q_B , p^{AP} , N^{BQ} , ΔH^F (heat of fusion); also to indicate the substance or phase to which the property refers p_A , p_B , v_L (volume of liquid), p_S (pressure of solid).

Italic numerals are used as subscripts to show specific cases. Thus, in changes of state and in integration, 1 and 2 always denote the initial and final states, respectively; in other cases they show merely different instances. In dealing with solutions, as above stated, the subscript zero shows the quantity to be a property of the pure solvent; absence of subscript to be that of the solution as a whole or of the solute; but to show that a solute is, or that all the solutes present are, at 1 *wm*. a superscript zero is attached to the symbol of the property, as in B^0 for molal boiling-point raising, or F^0 for the free energy of a solute when at 1 *wm*. (*Lewis, Randall*).

expressed as in the lower part of the table, is more conveniently used in fields of chemistry, like volumetric analysis, where volume measurements are involved, and in dealing with properties, like electrical conductance, whose values are primarily determined by space relations; also in many derivations involving kinetic molecular theories.

Prob. 1. — Relation of Weight and Volume Concentrations.

— At 25° a 9.47% solution of sulfuric acid (H_2SO_4) in water has a density 1.0603, and the density of water is 0.9971. Find the concentration of this solution, a , in weight-formality; b , in volume-formality at 25°; c , in weight-normality; d , in volume-normality at 25°.

Prob. 2. — Formal and Molal Concentrations Distinguished.

— In an aqueous solution 0.050 vf. in H_2SO_4 at 25° the acid has been found by physico-chemical measurements to be ionized to an extent of 65.6% into H^+ and HSO_4^- and to an extent of 34.4% into 2H^+ and $\text{SO}_4^{=}$. Find the volume-molalities of the chemical species H_2SO_4 , HSO_4^- , $\text{SO}_4^{=}$ and H^+ in the solution.

The molal concentration of particular species is conveniently shown by enclosing within parentheses the formula of the species; thus the molalities of various chemical species that may be present in a solution of sulfuric acid are denoted by the symbols (H_2SO_4), (H^+), (HSO_4^-), and ($\text{SO}_4^{=}$).

2. Properties Directly Related to the Molecular Theory and Their Thermodynamic Correlation. — As the mol-fraction of the solute in any solution approaches zero, the solution approaches a state known as that of a *perfect solution*. In this state some of its properties conform to simple laws, which, in analogy with the laws of perfect gases, may be called the *laws of perfect solutions*. These properties differ in the case of dilute solutions from those of the pure solvent by amounts which are determined primarily by the number, not by the nature, of the molecules of solute present per unit-weight of solvent. The principles relating to them are therefore important in the development of the *molecular theory*, and are useful for determining the *molecular state* of substances in solution.

The most important of these properties of solutions are their solute-vapor-pressure, solvent-vapor-pressure, boiling-point, freezing-point, and osmotic pressure. The laws relating to these properties of dilute solutions were for the most part dis-

covered by experimental investigation (largely by *Raoult*, 1883-1887); but the different properties and effects were later shown (*van't Hoff*, 1886) to be necessarily connected by purely thermodynamic relations.

In this book the laws relating to the vapor-pressure of the solvent and solute are made the basis of the thermodynamic presentation of the properties of solutions; but originally solute-vapor-pressure and osmotic pressure were used as the fundamental properties from which the others were derived (*van't Hoff*, 1886). This procedure is here followed because osmotic pressure is a less familiar and less simple property than that of vapor-pressure.

II. VAPOR-PRESSURE AND BOILING-POINT OF PURE SUBSTANCES.

3. Vapor-Pressure and Boiling-Point in General. — A liquid in contact with a vacuous space vaporizes until the pressure of its vapor in that space attains a perfectly definite value which is determined by the nature of the liquid and by the temperature. If, on the other hand, vapor having a pressure greater than this definite value is brought into contact with the liquid, condensation occurs until the pressure of the vapor falls to that value. In other words, for a given liquid at a given temperature there is only one pressure which its vapor can have and exist in equilibrium with that liquid. This pressure is called the *vapor-pressure* of the liquid at the specified temperature (*I*, 18). This is to be distinguished from the pressure of the vapor, which when not in contact with the liquid may have any value from zero up to one somewhat exceeding the vapor-pressure. Solids likewise have definite vapor-pressures, which with certain substances (like iodine) are appreciable even at room temperature.

The vapor-pressure of a liquid or solid substance increases rapidly with increasing temperature (Fig. 1; *I*, 18).

When a liquid or solid is in contact with a space containing a gas (for example, when water or iodine is in contact with an air space), approximately the same quantity of the liquid or solid vaporizes as if the gas were not present, provided the gas is only slightly soluble in the liquid, and provided its pressure is not much greater than one atmosphere. When the gas is readily soluble in the liquid, or when its pressure is large, large deviations from this principle may result.

Prob. 3. — Pressure-Volume Relations of Wet and Dry Gases. — 25 ml. of dry air at 28° and 1 atm. are collected over water, whose vapor-pressure at 28° is 28 mm. *a.* What is the pressure if the volume is still 25 ml.? *b.* What is the volume if the pressure is 1 atm.? *Ans. b,* 25.95 mm.

Prob. 4. — Vapor-Pressure Determined by an Air-Saturation Method. — 2000 ml. of dry air at 15° and 760 mm. are bubbled through bulbs containing a known weight of carbon bisulfide (CS_2) at 15°, and the mixture of air and bisulfide vapor is allowed to escape into the air at a pressure of 760 mm. By reweighing the bulbs, 3.011 g. of the bisulfide are found to have vaporized. Find the vapor-pressure of carbon bisulfide at 15°. *Ans.* 242 mm.

Prob. 5. — Vapor-Pressure Determined by Steam-Distillation. — A current of steam is passed at 1 atm. into a mixture of solid iodine (I_2) and water. The temperature of the distilling mixture is 98.4° . The escaping vapors are condensed, and the condensate is analyzed. It is found to contain 81.9 g. of iodine per 100 g. of water. Calculate the vapor-pressure of solid iodine at 98.4° .

Prob. 6. — Steam-Distillation of Very Volatile Substances Insoluble in Water. — Steam is bubbled through chlorobenzene (C_6H_5Cl) in a distilling flask; and the vapors, which escape under a barometric pressure of 1 atm., are condensed as a distillate. The steam partially condenses in the distilling flask, and brings the mixture of water and chlorobenzene (which are not appreciably soluble in one another) to that temperature where equilibrium prevails between the two liquid phases and the vapor phase. Determine this temperature and the mol-ratio (N_B/N_W) of the two components in the distillate with the aid of a plot of the following data, which represent the vapor-pressures of the pure substances at various temperatures:

	70°	80°	90°	100°
Water	234	355	526	760 mm.
Chlorobenzene	98	145	208	293 mm.

Prob. 7. — Steam-Distillation of Slightly Volatile Substances Insoluble in Water. — A mixture of water and nitrobenzene ($C_6H_5NO_2$) is distilled at 1 atm. by passing through it a current of steam. *a.* Calculate the temperature of the distilling mixture. *b.* Calculate the percentage by weight of nitrobenzene in the distillate. The vapor-pressure of water at 100° is 760 mm. and changes by 3.57% per degree; that of nitrobenzene at 100° is 20.8 mm. and changes by 4.2% per degree. *Ans. b, 15.7%.*

Note. — Distillation in a current of steam enables a slightly volatile substance to be vaporized and thus separated from non-volatile substances at a much lower temperature than that required to distil the mixture alone at barometric pressure. This is especially advantageous when the higher temperature may cause decomposition of the substances. A current of air would have the same result from a vapor-pressure viewpoint; but steam has the practical advantage that, upon cooling the distillate, the steam condenses with the volatile substance, so that this is not carried away as it might be by a current of air. Steam distillation can not be employed, however, when hot water causes decomposition of the substances present. A high-boiling liquid, like nitrobenzene, in which water is not very soluble can be effectively dried by passing a current of air through the heated liquid, by reason of the great difference in the vapor-pressures of the two non-miscible liquids.

The *boiling-point* of a liquid is the temperature at which it is in equilibrium with its vapor when both are subjected to any definite external pressure. In other words, it is the temperature at which the vapor-pressure, which increases as the temperature rises, becomes equal to the external pressure. When this temperature is slightly exceeded, assuming that there is no superheating, the vapor forms throughout the mass of the liquid (not merely at its free surface), giving rise to the familiar phenomenon of *boiling*.

4. Change of Vapor-Pressure and Boiling-Point with Temperature.—From the second law of thermodynamics expressions have been derived (II, 31) for the increase of the vapor-pressure p of a pure liquid with the temperature T , in terms of the heat-content increase ($\Delta\tilde{H}$) and volume-increase ($\tilde{v}_g - \tilde{v}_L$) that attend the reversible vaporization at T of one mol of the liquid. These expressions, called the *exact* and *approximate Clapeyron equations*, are as follows:

$$\frac{dp}{dT} = \frac{\Delta\tilde{H}}{T(\tilde{v}_g - \tilde{v}_L)}. \quad (1)$$

$$\frac{d \ln p}{dT} = \frac{\Delta\tilde{H}}{RT^2}. \quad (2)$$

The second equation becomes inexact as the vapor-pressure increases, because in deriving it from the exact equation the liquid volume $\tilde{v}_L$ was neglected and the gas volume $\tilde{v}_g$ was put equal to RT/p , the expression for it given by the perfect-gas equation.

By integrating Eq. 2 for the case that $\Delta\tilde{H}$ does not vary with the temperature, the following expression is obtained for the vapor-pressures p_g and p_l at two temperatures T_g and T_l :

$$\ln \frac{p_g}{p_l} = \frac{\Delta\tilde{H}}{R} \left(\frac{1}{T_l} - \frac{1}{T_g} \right) = \frac{\Delta\tilde{H}}{R} \left(\frac{T_g - T_l}{T_l T_g} \right). \quad (3)$$

Prob. 8. — Approximate Relation between Vapor-Pressure and Temperature.—*a.* By deriving the indefinite integral of Eq. 2 for the case that $\Delta\tilde{H}$ does not vary with the temperature, find the function of the vapor-pressure and that of the temperature which give a linear graph when plotted against each other. *b.* Make a large-scale plot of these functions, using the data for

water and for chlorobenzene previously given (Prob. 6; IV, 3).
c. From these data find and tabulate the ratios of the vapor-pressures at 85° and 75°, and 95° and 85°, for water and for chlorobenzene.

Note. — It will be seen that within a moderate range of temperature the vapor-pressure of a specified liquid increases by roughly equal multiples of its value for equal increments of temperature; and this multiple increase of vapor-pressure is found for different normal liquids (III, 29) (boiling say between 20° and 200°) to be of the same order of magnitude (thus 1.5 to 2.0 fold for each 10° rise in temperature).

Prob. 9. — Drying of a Gas by Cooling. — In order to decrease its humidity, moist air at 1 atm. is passed through a tube cooled to -25°. With the aid of the following data estimate the partial pressure of water-vapor in the issuing gas. The vapor-pressure of water is 9.21 mm. at 10° and 4.58 mm. at 0°; the heat of fusion of ice is 79.7 cal. per gram at 0°. Assume that the heat quantities involved do not vary with the temperature.

Since at the boiling-point of a liquid its vapor-pressure is equal to the external pressure upon the liquid and vapor, the Clapeyron equation also expresses (more clearly in inverted form) the change of boiling-point with the external pressure.

Prob. 10. — Effects of Pressure on Boiling-Point. — a. Calculate the boiling-point of water at 2 atm. under the assumption that within the temperature range involved $\Delta\tilde{I}$ is constant at its value at 100°, which is 9720 cal. b. Modify the approximate Clapeyron equation by eliminating this assumption with the aid of an empirical relation between heat of vaporization and temperature, and obtain a corresponding integrated expression.
Ans. a, 120.80° (observed 120.63°).

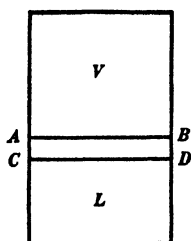
5. Vaporization Interpreted by the Kinetic Theory. —

When a liquid is placed in communication with an empty space, its molecules escape from its surface into the space above it till the vapor attains such a pressure that the number of molecules entering the liquid surface from the vapor side becomes equal to the number of molecules leaving the surface from the liquid side. When this occurs a *steady state*, constituting a condition of *equilibrium*, results; and the then prevailing pressure of the vapor equals the vapor-pressure of the liquid.

The kinetic principles underlying vaporization may be more fully developed by considering the factors that determine the number of molecules that pass through the surface in the two

directions. In Fig. 1 the line AB represents an imaginary plane above which the vapor V may be regarded as homogeneous, and the line CD represents another imaginary plane below which the liquid L may be regarded as homogeneous. In the intervening region $ABCD$, constituting the surface layer of the liquid, which in reality is of molecular dimensions, there is a progressive increase in the number of molecules per unit-volume from the number present in the vapor to the number present in the liquid.

FIGURE 1.



Now the molecules in the vapor, assuming it to be a perfect gas, exert no attraction upon one another; but between the molecules of the liquid, as between those of a gas at high pressure (*III*, 29), there is a large attraction. Within the main body of the liquid (below CD) there is, to be sure, no resultant attraction on any given molecule, since it is attracted equally in all directions by the uniformly distributed molecules surrounding it; but any molecule in the surface layer is evidently attracted downwards (into the liquid) in consequence of the greater concentration of the molecules in the layers below it. All the molecules that strike the plane AB from above (that is, from the vapor side) therefore have their downward velocities increased by the attraction, and pass into the liquid. Of the molecules that strike the plane CD from below (that is, from the liquid side) only those can traverse the surface layer and pass through the plane AB into the vapor which have an upward velocity great enough to overcome the downward attraction exerted by the molecules below. Hence, the number of molecules that escape from the liquid in unit-time is equal to the number (expressible by Maxwell's distribution law; *III*, 19) that pass up through the plane CD in unit-time with an upward velocity-component $\dot{x}_0$ great enough to overcompensate the decrease in upward velocity which any molecule experiences in passing from CD to AB , as a result of the molecular attraction. Finally, the number of molecules that must be present in unit-volume of the vapor in order that there may impinge on the plane AB in unit-time a number of molecules equal to that which escapes into the

vapor evidently determines the pressure of the vapor that is in equilibrium with the liquid at the temperature considered.

The great effect of temperature on vapor-pressure is likewise a consequence of these kinetic considerations. For the number of molecules which possess velocity-components greater than the limiting value permitting their escape into the vapor is shown by the Maxwell distribution law to increase very rapidly with the temperature.

The kinetic theory also accounts for the energy absorbed by the vaporization of a liquid at constant temperature and pressure. For, when any molecule of mass m passes from the liquid to the vapor, it evidently loses a quantity of kinetic energy $\frac{1}{2} m \bar{x}_0^2$ equal to that required to overcome the attraction of the other molecules. Consequently, the system would fall in temperature if it did not absorb from the surroundings an equal quantity of energy. The molar energy of vaporization $\Delta \tilde{E}$ is therefore expressed by the equation:

$$\Delta \tilde{E} = \frac{1}{2} \bar{n} m \bar{x}_0^2. \quad (4)$$

The application to these phenomena of the mathematical equations expressing Maxwell's distribution law leads to quantitative kinetic expressions for the vapor-pressure p of a pure liquid containing $\bar{n}$ molecules per unit-volume, each of mass m , and having a formular volume $\tilde{v}_L$ at temperature T and a molar weight M . The pressure is expressed in terms of the minimum value $\bar{x}_0$ of the upward velocity-component of its molecules or of its molar energy $\Delta \tilde{E}$ of vaporization, and of a factor $f(\tilde{v}_L)$ representing a molecule-velocity correction, which corresponds to, but is less definite than, the correction $\tilde{v}/(\tilde{v}-b)$ considered in the case of imperfect gases (III, 29). These expressions are:

$$p = \bar{n} f(\tilde{v}_L) k T e^{-\frac{m \bar{x}_0^2}{2 k T}} = \frac{f(\tilde{v}_L)}{\tilde{v}_L} R T e^{-\frac{\Delta \tilde{E}}{R T}}.$$

A striking result of these kinetic considerations is that the second of these expressions for the vapor-pressure, upon taking logarithms and differentiating with respect to temperature (neglecting any variation of $\tilde{v}_L$ or $\Delta \tilde{E}$), yields the Clapeyron equation (Eq. 2; IV, 4), which was independently derived from the laws of thermodynamics.

**** 6. Kinetic Derivation of Expressions for the Vapor-Pressure and Heat of Vaporization of Liquids.** — An equation for the vapor-pressure of a pure liquid containing only one molecular species may be mathematically derived in the way to be now described.

The method consists in finding an expression for the number n_L of molecules escaping in unit-time from unit-area of the upper boundary AB of the surface layer of the liquid (Fig. 1) and equating this with the previously found expression for the number n_0 of molecules impinging in unit-time upon that area from the vapor above.

The number n_L of molecules so escaping into the vapor is evidently equal to the number that in unit-time pass through unit-area of the lower boundary CD of the surface layer with an upward velocity-component $\dot{x}_i$ greater than the minimum value $\dot{x}_0$ which a molecule must have in order to overcome the force of attraction of the molecules beneath and pass through the surface layer into the vapor.

To derive an expression for this quantity n_L , we may first find expressions for the number of the molecules having velocities between $\dot{x}_i$ and $\dot{x}_i + d\dot{x}_i$ which lie beneath unit-area of the boundary CD within a (vertical) distance unity (1 cm.). Of the total number $\bar{n}$ of molecules (of mass m) in this unit-volume the number which possess upward velocity-components between $\dot{x}_i$ and $\dot{x}_i + d\dot{x}_i$ is found by multiplying this total number by the fraction of molecules shown by Maxwell's law to have this range of velocity-components (Eq. 35; III, 19). That is, the number of such molecules in unit-volume is:

$$\bar{n} \left(\frac{m}{2\pi kT} \right)^{0.5} e^{-(m\dot{x}_i^2/2kT)} d\dot{x}_i.$$

Of these molecules the number which pass upward in unit-time through unit-area of the boundary CD might be thought to equal this quantity multiplied by the upward velocity-component $\dot{x}_i$. This velocity-component is, however, the velocity between collisions; and, to find the actual number which pass upward in unit-time through unit-area of the liquid, the velocity $\dot{x}_i$ must be multiplied by a factor to account for the influence of the collisions. Since this influence probably depends not only on the size of the molecules, but also on their mutual attraction, and perhaps on other properties of the liquid medium, it can not be properly accounted for by a simple volume correction, like $\tilde{v}/(\tilde{v}-b)$ used in the case of imperfect gases, but a more general function $f(\tilde{v}_L)$ dependent on the molar volume $\tilde{v}_L$ and on the nature of the liquid must be introduced; this function being assumed only to have the

same value so long as the distance of the liquid molecules from one another remains constant.

Multiplying the last equation by $f(\tilde{v}_L) \dot{x}_i$ one gets the following expression for the number of liquid molecules dn_L with velocity-components between $\dot{x}_i$ and $\dot{x}_i + d\dot{x}_i$ which pass up through unit-area of the boundary CD in unit-time.

$$dn_L = \bar{n} f(\tilde{v}_L) \dot{x}_i \left(\frac{m}{2\pi kT} \right)^{0.5} e^{-(m\dot{x}_i^2/2kT)} d\dot{x}_i. \quad (5)$$

The number n_L of molecules that pass in unit-time unit-area of the boundary CD with upward velocity-components exceeding the minimum value $\dot{x}_0$ that permits their escape into the vapor is then obtained by integrating this equation between the limits 0 and n_L , $\dot{x}_0$ and ∞ . Assuming T and therefore $\tilde{v}_L$ constant, the resulting expression is:

$$n_L = \bar{n} f(\tilde{v}_L) \left(\frac{kT}{2\pi m} \right)^{0.5} e^{-(m\dot{x}_0^2/2kT)}. \quad (6)$$

On the other hand, the number n_g of molecules of the vapor captured by the liquid is equal to the total number which strike the boundary AB , since every molecule so striking is drawn in by the attraction of the liquid molecules beneath. However, for the number striking unit-area in unit-time an expression has been previously given (Eq. 19; III, 14). In accordance therewith one may write:

$$n_g = \frac{p}{(2\pi m kT)^{0.5}}. \quad (7)$$

From the condition that at equilibrium the number n_L of molecules escaping from the surface equals the number n_g entering it there result, on combining Eqs. 6 and 7 and replacing molecular by molar quantities, the following vapor-pressure expressions:

$$p = \bar{n} f(\tilde{v}_L) k T e^{-(m\dot{x}_0^2/2kT)}, \quad (8)$$

$$p = \frac{f(\tilde{v}_L)}{\tilde{v}_L} R T e^{-(M\dot{x}_0^2/2RT)}. \quad (9)$$

This equation expresses the vapor-pressure p of a normal liquid at any temperature T in terms of its molar weight M and molar volume $\tilde{v}_L$, and in terms of a quantity $f(\tilde{v}_L)$ which represents the shortening of the path of the molecules arising from collisions (due mainly probably to molecule volume and molecule attraction), and in terms of a second quantity $\dot{x}_0$ denoting the minimum velocity-component which enables them to escape from the surface of the liquid against the molecular attraction.

The foregoing kinetic considerations yield a simple expression also for the increase $\Delta \tilde{E}$ in energy-content that attends the isothermal vaporization of one mol of a liquid. This may be obtained by noting that each molecule which escapes from the body of the liquid into the vapor has its kinetic energy diminished by the amount $\frac{1}{2} m \dot{x}_0$. Hence, when $\tilde{n}$ molecules so escape, that is, when one mol of the liquid vaporizes, there is a decrease of $\frac{1}{2} \tilde{n} m \dot{x}_0^2$ in the kinetic energy of the system. This is attended by a corresponding fall of temperature; and, to restore the initial temperature, an equal amount of energy must be absorbed by the system. Hence:

$$\Delta \tilde{E} = \frac{1}{2} \tilde{n} m \dot{x}_0^2 = \frac{1}{2} M \dot{x}_0^2. \quad (10)$$

Substituting this value of $\frac{1}{2} M \dot{x}_0^2$ in Eq. 9, there results the following expression for the vapor-pressure:

$$p = \frac{f(\tilde{v}_L)}{\tilde{v}_L} R T e^{-\frac{\Delta \tilde{E}}{R T}} \quad (11)$$

By subjecting this equation to certain operations, it can be shown to lead to Clapeyron's approximate equation. Namely, by taking the logarithm of both members, one gets:

$$\ln p = \ln \frac{f(\tilde{v}_L)}{\tilde{v}_L} + \ln R T - \frac{\Delta \tilde{E}}{R T}.$$

And by differentiating this equation with respect to temperature, considering the variations of $f(\tilde{v}_L)/\tilde{v}_L$ and $\Delta \tilde{E}$ with the temperature to be of secondary magnitude, there results:

$$\frac{d \ln p}{dT} = \frac{\Delta \tilde{E} + R T}{R T^2} = \frac{\Delta \tilde{H}}{R T^2}. \quad (12)$$

Thus Clapeyron's equation, previously deduced from the second law of thermodynamics, has now been derived from the kinetic theory.

Prob. 11. — Molecular Magnitudes Derived from Kinetic Expressions for Heat of Vaporization and Vapor-Pressure. — The heat-content increase for the vaporization of one mol of benzene (C_6H_6) at its boiling-point (80.2°) at 1 atm. is 30 810 joules, and its density under these conditions is 0.815 g./ml. *a.* Calculate the minimum value $\dot{x}_0$ of the velocity-component of the molecules which permits them to escape from the surface of the liquid; also the ratio of the kinetic energy corresponding to this value to the mean kinetic energy ($\frac{3}{2} k T$) of each of the three rectangular components. *b.* Calculate the value of the factor $f(\tilde{v}_L)$ showing how many fold the collisions increase the factor $\dot{x}_0$, thereby increasing the number of molecules moving upwards through the liquid. *Ans. a.* Ratio, 19; *b.* 43.

**** 7. Heat of Vaporization of Normal Liquids.** — There remain to be mentioned two experimentally established relationships between the heats of vaporization of different normal liquids — those whose molecules show no association or aggregation. One of these principles states that for different normal liquids the ratio $\Delta\tilde{H}/T_p$ of the molar heat of vaporization $\Delta\tilde{H}$ to the temperature T_p at which the vapor-pressure attains some specified value, such as one atmosphere, has approximately (within a few percent) the same value (*Trouton, 1884*). And a second principle, considerably more exact, states that, in the case of different normal liquids, the ratio $\Delta\tilde{H}/T_c$ of the molar heat of vaporization $\Delta\tilde{H}$ to the temperature T_c at which the vapor acquires any specified molal concentration c or molar volume $\tilde{v}$ has very nearly the same value, lying mostly within 1% of the mean value for those of all normal substances. This last statement is subject to the provision that somewhat different constants be taken as characteristic of non-metallic and metallic substances. These principles, called *Trouton's rule* and *Hildebrand's rule*, are illustrated by Table II (*Hildebrand, 1915*), in which the data are expressed in calories and absolute temperatures.

TABLE II. HEATS OF VAPORIZATION OF LIQUIDS IN RELATION TO TROUTON'S AND HILDEBRAND'S RULES.

<i>Substance</i>	T_c	$\frac{\Delta\tilde{H}}{T_c}$ at $c = 0.00507$ or $\tilde{v} = 197.2 \text{ l.}$	T_p	$\frac{\Delta\tilde{H}}{T_p}$ at 100 mm.
Nitrogen	55	27.5	63	21.9
Oxygen	75	27.5	81	22.7
Chlorine	194	27.7	200	26.9
Pentane	256	26.9	260	26.3
Carbon tetrachloride	294	26.9	295	26.7
Benzene	298	27.3	299	27.3
Stannic chloride	329	27.1	328	27.1
Octane	338	27.5	339	27.7
Bromonaphthalene	486	27.5	472	28.1
Mercury	560	26.1	533	26.9
Cadmium	988	26.3	908	29.5
Zinc	1130	26.3	1030	30.0

It will be seen from Table II that for the non-metallic substances the values of $\Delta\tilde{H}/T_c$ are practically constant, though the temperatures vary from 55° to 486°A; but that the values of $\Delta\tilde{H}/T_p$ increase fairly steadily with the temperature, though not very rapidly after 200°A is reached. For the three metallic substances, as is true also for several other metals investigated (*Hildebrand, 1918*), the values at a specified vapor-concentration are also nearly identical with one another, though distinctly smaller (4%) than those for the non-metallic substances; whereas the values at the specified vapor-pressure, like those for non-metallic substances, increase markedly with the temperature.

Liquids that are not normal have a much larger heat of vaporization, presumably because the value includes the absorption of heat that attends the separation of the associated or aggregated molecules. Thus at $c = 0.00507$ the values of $\Delta\tilde{H}/T_c$ are 32.4, 32.0, and 33.4 for ammonia, water, and ethyl alcohol, whereas the average value is 27.4 for other substances. For such substances $\Delta\tilde{H}/T_p$ has similarly high values.

Prob. 12. — Application of Trouton's Rule to Normal Liquids. — At 1 atm. the boiling-point of benzene is 80.2° and its molar heat of vaporization is 7360 cal. Calculate the increase in the vapor-pressure of bromine per degree at its boiling-point, 59° at 1 atm.

III. SOLVENT-VAPOR-PRESSURE AND BOILING-POINT OF DILUTE SOLUTIONS.

8. Raoult's Law of the Vapor-Pressure of Dilute Solutions. — The vapor-pressure of a pure solvent is always lowered by dissolving in it another substance. As the mixture approaches the state of a perfect solution (that is, as the concentration of the solute approaches zero) the effect produced is quantitatively expressed by the following principle known as *Raoult's law*: The addition of a solute to a solvent causes at any temperature a fractional lowering of the vapor-pressure of the solvent equal to the mol-fraction X of the solute (*Raoult, 1887*). That is:

$$\frac{p_0 - p}{p_0} = \frac{N}{N_0 + N} = X. \quad (13)$$

Here p_0 is the vapor-pressure of the solvent in the pure state, and p is its vapor-pressure in a solution consisting of N mols of solute and N_0 mols of solvent. In this expression N_0 is equal to the weight m_0 of the solvent in the solution divided by its molecular weight M_0 in the vapor, and N is equal to the weight m of the solute divided by its molecular weight M in the solution. The value of M_0 is ordinarily that corresponding to the formula of the solvent; for the formula of a pure liquid is commonly so written as to represent the molecular weight of the substance in the gaseous state.

Raoult's law may also be stated in the following simple form, which indicates more clearly its significance. The vapor-pressure p of the solvent in a perfect solution is equal to its vapor-pressure p_0 in the pure state multiplied by the solvent-mol-fraction X_0 . That is:

$$p = p_0 X_0. \quad (14)$$

Raoult's law is applicable to dilute solutions in which the solute has an appreciable vapor-pressure, but in that case the partial vapor-pressure of the solvent in the solution, not the total vapor-pressure of the solution, must be considered.

The ratio of the vapor-pressures of solution and solvent is by Raoult's law determined only by the mol-fractions, and hence is independent of the temperature; that is, $p/p_0 = f(X_0) = f(X) \neq f(T)$.

Raoult's law is, as stated, in general to be regarded as a law of perfect solutions. It is found, however, that it holds true for many pairs of solvents and solutes up to fairly high solute concentrations — indeed, in some cases throughout the whole range of concentration. Solutions whose solvent-vapor-pressure conforms to Raoult's law up to any considerable solute-mol-fraction are here often called for short *Raoult-law solutions* (up to that mol-fraction). The properties of such solutions are considered in the successive sections of this Chapter; being treated as a second ideal type of solutions, supplementary to and including perfect solutions.

**** Kinetic Interpretation of Raoult's Law.**

A kinetic interpretation of Raoult's law in its most general aspect can readily be given, though this is by no means true with respect to some of its detailed features, as will be seen from the following considerations. Like any vapor-pressure law, Raoult's law must relate fundamentally to the distribution between the liquid phase and vapor phase of the chemical species or kind of molecule which gives rise to the partial pressure of the vapor. Where the liquid solvent is normal, that is, contains only a single kind of molecule, there is obviously only one chemical species involved in the liquid-vapor distribution; and the kinetic equations previously obtained for the vapor-pressure of a normal liquid can be used for deriving Raoult's law for solutions in which such a liquid is the solvent, provided certain assumptions can be made in the case of small solute concentrations.

Now the equation

$$p = \bar{n} f(\tilde{v}_L) k T e^{-(m\dot{x}_0^2/2kT)} \quad (\text{Eq. 8; IV, 6})$$

shows that the solvent-vapor-pressure p of such solutions is equal to the vapor-pressure p_0 of the pure solvent multiplied by the ratio of the number of solvent molecules in unit-volume of the solution to the number of them in unit-volume of the pure solvent, in case it be assumed that the addition of solute is not large enough to change appreciably the value of the collision correction $f(\tilde{v})$ or that of the limiting velocity-component $\dot{x}_0$ that permits escape of the solvent molecules from the surface of the liquid. This molecule-ratio, moreover, is the mol-ratio of the solvent in the solution provided the replacement of a small proportion of the solvent by solute does not cause appreciable change in volume. Hence Raoult's law is a consequence from the general vapor-pressure equation provided these three factors (collision-correction $f(\tilde{v})$, limiting velocity-component $\dot{x}_0$, and volume v of the solution) be not appreciably changed.

It is obvious that these factors would commonly be changed by the addition of a large proportion of solute, so that as a general principle Raoult's law will be confined to dilute solutions. Moreover, even a small addition of solute *may* change these factors by an amount appreciable in comparison with the change in solvent-mol-fraction. This derivation of Raoult's law is therefore not rigorous, even for perfect solutions. Conversely, however, the validity of Raoult's law is inductive evidence of the actual negligibility of these factors at small solute-mol-fractions, or of the compensation of the factors by one another.

In case the pure solvent is partially associated, as in the case of water, so that it contains two or more kinds of molecules, it is also not evident that Raoult's law is a consequence of the general vapor-pressure equations, though experimental investigations show that in fact this molecular condition of the solvent does not limit the validity of the law.

Kinetic interpretations will be more fully considered in connection with the deviations from Raoult's law.

***** Raoult's Law when the Vapor Is Imperfect.***

In case the pressure of the vapor does not conform to the perfect-gas laws, but to the equation of state $p\tilde{v}(1-\beta p) = RT$, the expression of Raoult's law should be corrected so as to read as follows:

$$\frac{p}{(1-\beta p)} = X_0 \frac{p_0}{1 - \beta p_0} \quad (15)$$

Prob. 13. — Derivation of the Corrected Raoult's Equation.— Consider the following isothermal reversible process at T by which 1 mol of a pure solvent at vapor-pressure p_0 is added to a very large (theoretically infinite) quantity of a solution of vapor-pressure p with solvent-mol-fraction X_0 : Vaporize the solvent at pressure p_0 , expand the vapor to pressure p , and condense the vapor at this pressure into the solution (whose mol-fraction remains constant because of its large volume). *a, b.* Find the free-energy decrease $-\Delta F$ attending this process, assuming, *a*, that the pressure of the vapor conforms to the perfect-gas equation, *b*, that it conforms to the equation of state $p\tilde{v}(1-\beta p) = RT$ (using Eq. 43, Table IV; II, 23). *c.* Derive from the usual form of Raoult's law and from the result found in *a* (when the vapor was in the perfect-gas state) an expression for the free-energy decrease in terms of the solvent-mol-fraction X_0 of the solution. *d.* Noting that this free-energy decrease (attending the change of a substance from the pure liquid state to the dissolved state) can not depend on a characteristic of the vapor, such as its equation of state, derive the corrected Raoult equation (Eq. 15).

9. Verification of Raoult's Law and Its Use in Determining Molecular Weights. — For measurement of the vapor-pressure lowering caused by non-volatile solutes three types of methods have been frequently employed:

(1) Evaporation of the solvent from the pure solvent and from various solutions into a vacuous space in an apparatus so designed that the solvent and the solutions are kept at exactly the same temperature, and the vapor-pressures or the vapor-pressure differences are measured with a precision type of manometer.

(2) Saturation of a definite quantity of air with solvent-vapor by passing air through the pure solvent and through the solutions kept at some definite temperature; with determination (as in Prob. 4; IV, 3) of the weights of the solvent that are vaporized from the pure solvent and from the solutions.

(3) Boiling of the pure solvent and the solutions in separate experiments under pressures which are so adjusted that the boiling takes place in each case at exactly the same temperature, and precise measurement of these pressures.

Few precise measurements of the vapor-pressure of dilute solutions of unionized solutes exist which can be used to test the degree of validity of Raoult's law at small concentrations. Table III contains the results of a series of such measurements with mannite in water (*Frazer, Lovelace, Rogers, 1920*) obtained by the first of the just described methods. The conformity with Raoult's law is seen to be remarkably close — closer at the higher mol-fractions than with most substances. Furthermore, these results confirm the conclusion that Raoult's law holds for dilute solutions even when the solvent molecules are largely associated.

TABLE III. VALIDITY OF RAOULT'S VAPOR-PRESSURE LAW FOR AQUEOUS SOLUTIONS OF MANNITE AT 20°.

p_0 = Vapor-Pressure of Pure Water, 17.51 mm.

$100 X$	$\frac{p_0 - p}{p_0 X}$	$100 X$	$\frac{p_0 - p}{p_0 X}$
0.18	0.991	1.23	1.001
0.53	0.992	1.41	1.005
0.71	0.993	1.58	1.0086
0.88	0.995	1.75	1.0080
1.06	1.002	—	—

Raoult's law applied to solutions of small concentration affords a method of determining approximately the molecular weights of solutes, and the molecular states in which they exist in solution. The method has not been extensively used, however, because in dilute solutions the vapor-pressure lowering is so small as to make it difficult to get precision, and because in more concentrated solutions theoretical deviations from the law exist. Moreover, other more convenient, thermodynamically related, methods exist, namely, the determination of the raising of the boiling-point or lowering of the freezing-point of solvents by solutes. However, the vapor-pressure method has proved useful in some cases, as in determining the molecular weights of other metals dissolved in mercury (a high-boiling and low-freezing solvent).

Prob. 14. — Molecular Formulas of Metals in Mercury Solution. — Three atwt. of various metals when dissolved in 97 atwt. of mercury give at the boiling-point of mercury (357°) solutions that have the following mercury vapor-pressures, expressed in atmospheres (*Ramsay, 1889; Beckman, Liesche, 1914; I.C.T., 3, 284*).

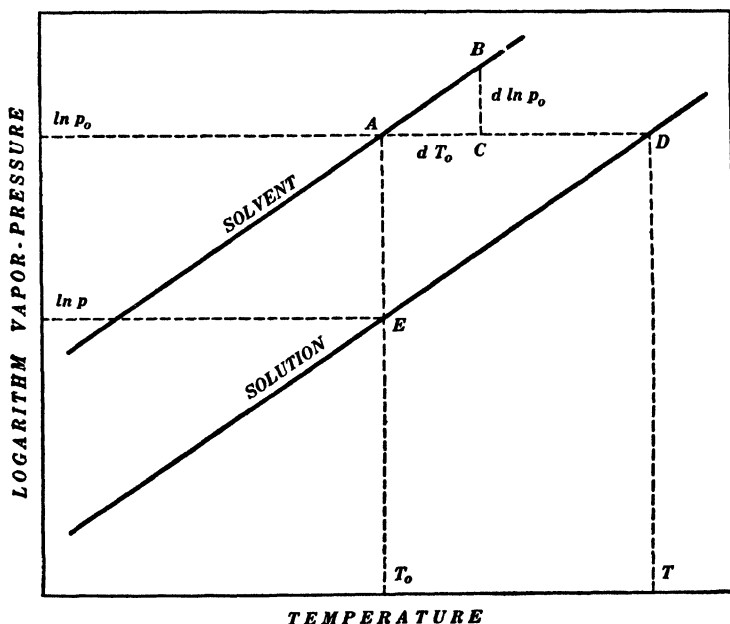
Ag	Au	Bi	Ca	Cd	K
0.972	0.975	0.976	0.955	0.968	0.950
Mg	Na	Pb	Sn	Tl	Zn
0.964	0.962	0.976	0.976	0.969	0.971

a. State what these results indicate as to the molecular state of these metals in the liquid amalgams. *b.* Discuss explanations of the low vapor-pressures of the calcium, potassium, magnesium, and sodium amalgams, taking into account the facts that the vapor-pressures of solutions of 1 atwt. of them in 99 atwt. of mercury are 0.988, 0.987, 0.988, and 0.989 atm., respectively.

10. Laws of Boiling-Point Raising: Its Relation to Vapor-Pressure Lowering and Molar Composition. — Since the addition of a non-volatile solute to a pure solvent at any temperature lowers the vapor-pressure of the solvent, it is obvious that the temperature at which the vapor-pressure becomes equal to any specified external pressure is higher for the solution than for the pure solvent — in other words, that the boiling-point of the solvent is raised by the addition of a non-volatile solute. Precise methods of determining this boiling-point raising were early perfected (*Beckmann, 1889*); and its magnitude was found experimentally to be proportional to the number of mols of solute per unit-weight of solvent at small solute concentrations.

The theoretical relation between the increase in the boiling-point and the decrease in the vapor-pressure of a solvent produced by a non-volatile solute can be obtained graphically from a plot of the observed vapor-pressures of the pure solvent and of the solutions at different temperatures; or this relation can be derived mathematically by properly interpreting the expression for the effect of temperature on vapor-pressure given by Clapeyron's equation.

FIGURE 2. VAPOR-PRESSURE-TEMPERATURE DIAGRAM FOR BOILING-POINTS.



Consider Fig. 2, in which the natural logarithms of the vapor-pressures of a pure solvent and of a solution containing a non-volatile solute at mol-fraction X are plotted against the temperature; the logarithms being used, rather than the pressures themselves, since then the graphs may be regarded as straight lines for dilute solutions. In this figure the boiling-points T_0 and T of the pure solvent and of the solution under some externally applied pressure p_{Δ} (whose logarithm is shown by the upper horizontal line) are given by the intersections of the vapor-

pressure graphs with that line; and the logarithms of the two vapor-pressures p_0 and p at the boiling-point T_0 of the pure solvent under the pressure p_{at} are given by the ordinates at the abscissa T_0 . Now it is evident that the boiling-point increase $T - T_0$ produced by the solute is equal to the increase in temperature required to raise the vapor-pressure of the solution from p to p_{at} (equal to p_0); and that this increase may be found when the change of the vapor-pressure of the solution with temperature is known, namely, by plotting the corresponding graph for the solution between the points whose coordinates are $\ln p$, T_0 and $\ln p_0$, T , and reading off the difference in the abscissas of these points.

Inasmuch as vapor-pressure-temperature curves are more commonly known for pure solvents than for solutions, it is important to note that, in case the vapor-pressure lowering is small, the vapor-pressure-temperature curve for the pure solvent is substantially parallel with that for the solution, and therefore the boiling-point raising $T - T_0$ can be evaluated by using the solvent curve.

It follows then from the geometrical relations of Fig. 2, namely, from the similarity of the triangles ABC and DEA, that the slope $\partial \ln p_0 / \partial T$ of the logarithmic vapor-pressure-temperature curve of the solvent is equal to the natural logarithm of the two vapor-pressures $\ln (p_0/p)$ divided by the corresponding boiling-point raising $T - T_0$, provided the solution is so dilute that this curve can be regarded as a straight line. That is, for solutes at small mol-fraction:

$$T - T_0 = \frac{\partial T}{\partial \ln p_0} \ln \frac{p_0}{p}. \quad (16)$$

By writing $-\ln [1 - (p_0 - p)/p_0]$ for $\ln (p_0/p)$, developing this in a series by Maclaurin's theorem, and neglecting the higher powers of $(p_0 - p)/p_0$, which is permissible when this quantity is very small, one obtains for solutes at small mol-fraction:

$$T - T_0 = \frac{\partial T_0}{\partial \ln p_0} \frac{p_0 - p}{p_0}. \quad (17)$$

This evidently expresses the principle that the boiling-point raising of any dilute solution is proportional to its fractional

vapor-pressure lowering, the proportionality-constant being the reciprocal of the fractional increment of the vapor-pressure of the *pure solvent* per degree of temperature.

Replacing in this equation (Eq. 17) the fractional increase in the vapor-pressure of the solvent per degree by the expression for it given by the approximate Clapeyron equation yields the following relation between the boiling-point raising and fractional vapor-pressure lowering caused by any solute at small concentration, in terms of the molar heat of vaporization $\Delta\tilde{H}_0$ of the solvent at T_0 :

$$T - T_0 = \frac{R T_0^2}{\Delta\tilde{H}_0} \frac{p_0 - p}{p_0}. \quad (18)$$

Substitution in Eqs. 17 and 18 of the solute-mol-fraction X for the fractional vapor-pressure lowering in accordance with Raoult's law (IV, 8), and replacement of X by the mol-ratio N/N_0 (practically equivalent to it in very dilute solution) lead to the following equations:

$$T - T_0 = \frac{\partial T_0}{\partial \ln p_0} X = \frac{\partial T_0}{\partial \ln p_0} \frac{N}{N_0}. \quad (19)$$

$$T - T_0 = \frac{R T_0^2}{\Delta\tilde{H}_0} X = \frac{R T_0^2}{\Delta\tilde{H}_0} \frac{N}{N_0}. \quad (20)$$

These equations show that a non-volatile solute, as its mol-fraction approaches zero, causes, independent of its nature, a raising of the boiling-point of the solvent that is proportional to the number of mols of solute per formula-weight of solvent, and they express the proportionality-constant in terms of either of two different properties of the pure solvent. The so-expressed principle is the *law of boiling-point raising for perfect solutions*.

A more rigorous analysis (IV, 13) leads to the following expressions, which for any solution that conforms to Raoult's law give closely approximate results up to even a fairly large solute-mol-fraction:

$$T - T_0 = -\frac{R T T_0}{\Delta\tilde{H}_0} \ln (1-X). \quad (21)$$

$$T - T_0 = \frac{R T T_0}{\Delta\tilde{H}_0} \ln \left(1 + \frac{N}{N_0} \right). \quad (22)$$

The precise values of X and of N/N_0 that correspond to certain values of $-\ln(1-X)$ are as follows:

$-\ln(1-X)$	0.0200	0.0400	0.0700	0.1000
X	0.0198	0.0392	0.0676	0.0952
N/N_0	0.0202	0.0408	0.0725	0.1052

It will be seen that the use of the two approximations X and N/N_0 gives boiling-points that deviate in opposite directions from those corresponding to Raoult's law; also that these deviations become large if the dilute-solution equations be used for even fairly concentrated solutions (thus 5½% at 10 mol-percent of solute). Still larger deviations may arise because such solutions do not conform to Raoult's law.

11. Experimental Determination of Boiling-Point Constants. — The ratio of the boiling-point raising to the mol-ratio N/N_0 approaches a constant characteristic of the solvent as that mol-ratio approaches zero (Eqs. 19, 20). This may be called its *mol-ratio boiling-point raising* B_0 ; for it is evidently the boiling-point raising per mol of solute in one mol of solvent.

With the aid of this constant the laws of boiling-point raising for perfect solutions may be summarized by the following equations, in which B_0 may here represent specifically the empirical value obtained from boiling-point raising measurements:

$$\frac{T - T_0}{N/N_0} = B_0 = \frac{1}{(d \ln p_0)/dT_0} = \frac{R T_0^2}{\Delta \tilde{H}_0}. \quad (23)$$

In correspondence with these equations the mol-ratio boiling-point raising can be derived from three kinds of experiments:

(1) From the rises in boiling-point produced by definite weights of solutes of known molecular weight dissolved in a definite weight of the solvent, extrapolated to zero mol-ratio.

(2) From the change of the vapor-pressure of the pure solvent with the temperature.

(3) From the molar heat of vaporization of the solvent determined directly by calorimetric measurements.

In chemical literature is often recorded, not this boiling-point constant, but another constant, called the *molal boiling-point raising* B^0 , which is the boiling-point raising per mol of solute in 1000 grams of solvent. It may also be defined as the value approached by $(T - T_0)/c$, as the weight-molality c approaches zero; and the general magnitude of the effect of solutes

on the boiling-point of a solvent is shown by the fact that its molal boiling-point raising is roughly equal to the actual boiling-point raising in its 1.0 weight-molal solutions. The value of this constant can obviously be readily calculated from that of the mol-ratio boiling-point raising.

Prob. 15. — Relation between the Mol-Ratio Boiling-Point Raising and the Molal Boiling-Point Raising. — *a.* Calculate the molal boiling-point raising (in degrees per mol per kg.) for water from its mol-ratio boiling-point raising, which is 28.46° per mol per mol. *b.* Formulate the algebraic relation between the two constants.

Prob. 16. — Methods of Evaluating Boiling-Point Constants. — Calculate the molal boiling-point raising for carbon bisulfide from the following data: *a.* The boiling-point of a solution of 3.20 g. of naphthalene ($C_{10}H_8$) in 50 g. of carbon bisulfide is 1.17° higher than that of the pure solvent. *b.* From the vapor-pressure-temperature curve of carbon bisulfide its vapor-pressure is found to increase 24.7 mm. per degree at its boiling-point (46.25°) at 1 atm. *c.* The heat of vaporization of one gram of carbon bisulfide at its boiling-point (46.25°) is 84.1 cal. *Ans.* *a.*, 2.34; *b.*, 2.34; *c.*, 2.41.

Table IV contains for a few important solvents values of the molal boiling-point raising derived by the three experimental methods mentioned above; namely, from actual boiling-point raisings (*I.C.T.*, 3, 324; 1928), from calorimetric heats of vaporization $\Delta\tilde{H}_0$ of pure solvents (*I.C.T.*, 5, 138; 1929), and from the temperature-coefficient dp_0/dT_0 of their vapor-pressures (*Rosanoff, Dunphy, 1914*).

TABLE IV. MOLAL BOILING-POINT RAISING.

		Water H_2O	Ethyl Ether $C_4H_{10}O$	Ethyl Alcohol C_2H_5OH	Ben- zene C_6H_6	Carbon Tetra- chloride CCl_4
Boiling-Point (t_0) at 1 atm.		100.00	34.6	78.3	80.2	76.75
Method	Limit of $(T - T_0)/c$	0.520	2.16	1.20	2.62	4.83
	Calorimetric $\Delta\tilde{H}_0$	0.5127	2.24	1.20	2.629	5.24
	From dp_0/dT_0	0.518	2.21	1.24	2.58	5.05

The accuracy of the constants derived from $\Delta\tilde{H}_0$ is estimated at 0.1% for water and benzene, at 0.3% for carbon tetrachloride, at 2% for ether, and at 4% for ethyl alcohol. The results from dp_0/dT_0 are corrected for imperfection of the vapor (*IV, 13*).

12. Molecular State of Dissolved Substances Determined from Their Effects on Boiling-Point. — From any observed raising of the boiling-point of a solvent and from either of its boiling-point raising constants there may be calculated the number of mols of dissolved substance present in the number of grams of it taken for the experiment. The law of boiling-point raising, like Raoult's law of vapor-pressure lowering from which it is derived, therefore enables the molecular state of substances in solution to be determined.

Prob. 17. — Molecular Weight and Molecular Formula of an Organic Substance. — *a.* When 1.06 g. of a substance are dissolved in 74 g. of ether ($C_4H_{10}O$) its boiling-point is raised 0.284° . Find the molecular weight of the substance. *b.* The substance is a hydrocarbon containing 90.50 % of carbon. Find its molecular formula.

Prob. 18. — Molecular State of the Same Substance in Different Solvents. — A solution of 12.2 g. of benzoic acid in 100 g. of ethyl alcohol boils 1.13° higher than pure ethyl alcohol (*Beckmann, 1890*). A solution of 12.2 g. of benzoic acid in 100 g. of benzene boils 1.36° higher than pure benzene (*Innes, 1902*). Calculate the molecular weight of benzoic acid in each of these solvents; and specify what the results show about its molecular state in each solvent. Its composition by weight is expressed by $C_6H_5CO_2H$. *Ans.* 129 and 236.

Prob. 19. — Molecular Formula of Phosphorus in Carbon Bisulfide. — *a.* Find the molecular weight of phosphorus in carbon bisulfide solution corresponding to the following data. The molal boiling-point raising for carbon bisulfide at its boiling-point (46.25°) is 2.40. The boiling-point of 100 g. of solvent is raised 1.054° by dissolving in it 6.20 g. of phosphorus, and 1.885° by dissolving in it 12.41 g. of phosphorus (*Beckmann, 1890*). *b.* Justify by extrapolation the conclusion that its molecular formula is probably P_4 in very dilute solution.

Prob. 20. — Compound Formation in Solution. — Find how much higher than the boiling-point of pure CS_2 that of each of the following solutions will be: *a.* solution of 1.55 g. of phosphorus (P_4) in 100 g. of CS_2 ; *b-e.* this solution with 1.27 g. of I_2 added to it, *b.* if the iodine remains uncombined; *c.* if it all combines forming P_4I_6 ; *d.* if it all combines forming P_2I_4 ; *e.* if it all combines forming PI_3 .

Notes. — The vapor-density found for phosphorus at $500^\circ C$ corresponds to a molecular weight of 126.1, equal to 4.07 times its atomic weight. The formula of phosphorus iodide is in fact P_2I_4 .

Prob. 21. — Molecular State of Sulfur in Carbon Bisulfide

Solution. — A solution of 3.795 g. of sulfur in 100 g. of carbon bisulfide (molal boiling-point raising, 2.40) has been observed to boil 0.361° higher than pure carbon bisulfide (*Sakurai, 1892*).

a. Calculate the molecular weight of sulfur in carbon bisulfide.

b. State what conclusion can be drawn from this result as to the nature of the sulfur molecules in this solvent. *Ans. a, 252.*

Note. — In 2.00% and 6.26% solutions of sulfur in CS_2 255 and 255 were found as its molecular weights, equal to 8.0 times its atomic weight.

**** 13. Analytic Derivation of the Boiling-Point Equation for Solutions Conforming to Raoult's Law.** — The exact relations between the vapor-pressure lowering, boiling-point raising, and molar composition of Raoult-law solutions can be derived by the following analytic method.

Consider that the vapor-pressure p of a solution containing a particular (non-volatile) solute in a particular solvent is fully determined by the mol-fraction X of the solute and by the temperature T ; that is, $p = f(X, T)$. Hence any variation dp in its vapor-pressure is the sum of the effects produced by the separate changes dX and dT in these variables. That is, in partial derivative notation (*I, 13*):

$$dp = \left(\frac{\partial p}{\partial X} \right)_T dX + \left(\frac{\partial p}{\partial T} \right)_X dT. \quad (24)$$

Consider now that the vapor-pressure p of the solution was originally equal to the applied pressure p_{ap} , so that the solution was at its boiling temperature T ; consider also that, after the infinitesimal change dX in the mol-fraction of solute has taken place, the temperature-change dT is made such that the solution is still at its boiling-point, now $T + dT$, at the same applied pressure. This will be true only in case the decrement in the vapor-pressure produced by increasing only the mol-fraction of the solute by dX just compensates the increment in vapor-pressure produced by increasing only the temperature by dT so that the total vapor-pressure change dp is zero. But then Eq. 24 becomes:

$$\left(\frac{\partial p}{\partial X} \right)_T dX + \left(\frac{\partial p}{\partial T} \right)_X dT = 0. \quad (25)$$

Evidently dT now represents the rise in boiling-point of the solution due to an increase in the mol-fraction of the solute, under the constant applied pressure p_{ap} . For the ratio dT/dX may therefore be written $(\partial T/\partial X)_{p_{\text{ap}}}$, whereby Eq. 25 becomes:

$$\left(\frac{\partial T}{\partial X}\right)_{p, p} = - \frac{(\partial p / \partial X)_T}{(\partial p / \partial T)_X}. \quad (26)$$

Clapeyron's equation (Eq. 2) and differentiation of Raoult's equation (Eq. 13) yield expressions for the last two partial derivatives. By substitution of these expressions in Eq. 26 there results:

$$\left(\frac{\partial T}{\partial X}\right)_{p, p} = \frac{R T^2}{\Delta \tilde{H}_X} \frac{p_0}{p}; \quad \text{or} \quad \frac{dT}{T^2} = \frac{R}{\Delta \tilde{H}} \frac{p_0}{p} dX. \quad (27)$$

Replacing p_0/p by $1/(1-X)$ from Raoult's equation yields:

$$\frac{dT}{T^2} = \frac{R}{\Delta \tilde{H}} \frac{dX}{1-X}. \quad (28)$$

In these expressions $\Delta \tilde{H}$ or $\Delta \tilde{H}_X$ is the heat absorbed by the vaporization of one mol of the solvent out of a solution with solute-mol-fraction X at temperature T ; an infinite quantity being considered so that there be no change in its composition during the vaporization of one mol. But it can be shown that the heat of vaporization $\Delta \tilde{H}$ of the solvent out of a solution that conforms to Raoult's law must be equal to the heat of vaporization $\Delta \tilde{H}_0$ of the pure solvent at the same temperature, so that $\Delta \tilde{H}$ may be replaced by $\Delta \tilde{H}_0$ in Eq. 28, yielding the expression:

$$dT = - \frac{R T^2}{\Delta \tilde{H}_0} d \ln (1-X). \quad (29)$$

That these two heats of vaporization are equal follows from Raoult's law, according to which the ratio p_0/p is fully determined by the mol-fraction — a fact which corresponds to the requirement that $\partial \ln p_0 / \partial T$ equal $\partial \ln p / \partial T$ at any given temperature; and this in turn, in virtue of the Clapeyron equations for the solvent and solution, evidently implies equality of $\Delta \tilde{H}_0$ and $\Delta \tilde{H}$.

Moreover, Eq. 28 is not made inexact by deriving $(\partial p / \partial T)_X$ from the approximate Clapeyron equation (except for the error, very small at moderate vapor-pressures, caused by neglecting the molar volume of the liquid in Clapeyron's exact equation). For it will now be shown that the approximation so introduced into Eq. 27 was compensated by the use of Raoult's ordinary equation $p = p_0 X_0$. Namely, if the equation of state of the vapor is $p \tilde{v} (1-\beta p) = R T$, Clapeyron's exact equation (neglecting $\tilde{v}_L$) becomes:

$$\frac{dp/p}{dT} = (1-\beta p) \frac{\Delta \tilde{H}}{R T^2}. \quad (30)$$

And if Raoult's equation be corrected to correspond to this equation of state, it yields upon differentiation:

$$\frac{dp/p}{dX} = - (1-\beta p) \frac{1}{1-X}. \quad (31)$$

Hence, on finding an expression for $(\partial T)/(\partial X)_{p_{AP}}$ from Eq. 25, the correction-factor $1 - \beta p$ for the deviation of the vapor from the perfect-gas state drops out, and the same expression as before (Eq. 28) results.

In order to integrate Eq. 29 exactly, the heat-content increase $\Delta \tilde{H}_0$ must first be expressed as a function of the temperature (such as $\Delta \tilde{H}_0 = \Delta \tilde{H}'_0 + \alpha T$). However, this effect is small for the small temperature-interval commonly involved in applications of the equation to boiling-point raising; thus the heat of vaporization of water is only 1.2% less at 110° than at 100°. Consequently the equation may usually be integrated without serious error under the assumption that $\Delta \tilde{H}_0$ is constant (especially if a value at a temperature midway between T and T_0 be used). In that case there results the expression:

$$T - T_0 = - \frac{R T T_0}{\Delta \tilde{H}_0} \ln (1-X). \quad (32)$$

This is the equation that was previously cited (Eq. 21). It gives the exact boiling-point raising for any solution whose vapor-pressure conforms to Raoult's law up to the solute-mol-fraction X , except for the small errors involved in neglecting the volume $\tilde{v}_L$ of the liquid in Clapeyron's equation and in considering $\Delta \tilde{H}_0$ to be constant between T and T_0 .

Prob. 22. — Analytic Derivation of the Boiling-Point Equation. — Formulate the successive steps by which the final equation for the boiling-point raising of a Raoult-law solution (Eq. 32) has been deduced from the general partial-derivative equation (Eq. 24).

Prob. 23. — Proof of the Equality of the Heats of Vaporization of a Pure Solvent and Its Raoult-Law Solution. — Starting with Raoult's law expressed by the functional equation $p_0/p = f(X)$ and using approximate Clapeyron equations, write a series of expressions which shows the equality of the molar heats of vaporization $\Delta \tilde{H}_0$ and $\Delta \tilde{H}$ of a solvent in the pure state and out of a Raoult-law solution.

IV. FREEZING-POINT OF DILUTE SOLUTIONS.

14. Freezing-Point of Solutions in General. — The *freezing-point* of a liquid is that temperature at which the solid solvent exists in equilibrium with the liquid solvent or solution (I, 18). In order to establish rapidly this equilibrium, it is essential that there be a large surface of contact between the two phases. In precise measurements this is secured by mixing a large quantity of the fine solid with the solution.

The solid which separates from the solution consists commonly of the pure solvent-substance; and this is assumed to be the case throughout the following considerations. However, this is by no means always the case; for the solid which crystallizes out of the freezing solution is sometimes a *solid solution* — a physically homogeneous solid mixture which contains no larger aggregates than the molecules of the component substances. This is especially common with mixtures of metals (alloys); and the freezing-point laws presented in this section can be safely applied to an alloy only when there is evidence that the solid phase consists of a pure metal.

Thermodynamically, the freezing-point lowering by solutes is related to their vapor-pressure lowering; and the laws of the one property can be derived from those of the other. This is based on the fundamental law, previously derived (II, 25) from the perpetual-motion principle, that when a liquid and a solid phase are at equilibrium, the vapor-pressures of any substance present in the two phases are equal. Thus when a solution is at its freezing-point, the solvent-vapor-pressure of the solution is equal to that of the ice.

From this law the following simple principles about freezing-point can be at once derived. Solutions containing those quantities of different solutes in a specified solvent which at a given temperature have the same solvent-vapor-pressure have also the same freezing-point; and dilute solutions with equal mol-fractions of solute, since they have, in virtue of Raoult's law, the same vapor-pressure, have also the same freezing-point. Moreover, from the slopes and intersections of the vapor-pressure-temperature curves of solutions and of the solid solvent (Fig. 3; IV, 18) the lowering of freezing-point for dilute solutions can be quantitatively determined.

15. Law of Freezing-Point Lowering for Perfect Solutions. — By direct measurements with solutions of unionized substances a principle was early discovered (*Raoult, 1883*), analogous in form to the law of boiling-point raising, which may be called the *law of freezing-point lowering of perfect solutions*. This states that a solute, regardless of its nature, causes a lowering of the freezing-point $T_0 - T$ of any given solvent which, as the solute-mol-fraction approaches zero, becomes proportional to the number of mols of solute per formula-weight of solvent, or to the weight-molality c of the solute. That is, representing by G_0 and G^0 two constants characteristic of the solvent, called the *mol-ratio freezing-point lowering* and the *molal freezing-point lowering*, respectively, this law is expressed by the equations:

$$T_0 - T = G_0 \frac{N}{N_0} \quad (32); \quad T_0 - T = G^0 c. \quad (33)$$

Furthermore, as described below, Raoult's law and Clapeyron's equation show that the proportionality-constant may be formulated in terms of the molar heat of fusion $\Delta\tilde{H}_0^f$ of the solvent and of its freezing-point T_0 (*van't Hoff, 1886*). The law of perfect solutions is therefore also expressed by the following equation:

$$T_0 - T = \frac{R T_0^2}{\Delta\tilde{H}_0^f} \frac{N}{N_0}. \quad (34)$$

Mathematical analysis (*IV, 19*) shows that the freezing-point lowering, like the boiling-point raising, for Raoult-law solutions is given, up to fairly large solute-mol-fractions, with substantial accuracy by the equation:

$$T_0 - T = - \frac{R T T_0}{\Delta\tilde{H}_0^f} \ln (1 - X). \quad (35)$$

16. Experimental Determination of Freezing-Point Constants. — The values of the constants have been practically determined from the two following kinds of experimental data in accord with Eqs. 32, 33, and 34, with concordant results.

(1) From the falls in freezing-point produced by definite weights of solutes of known molecular weight in a definite weight of the solvent, with extrapolation to zero mol-ratio or molality.

(2) From the calorimetric heat of fusion of the solvent.

For a few important solvents values of the molal freezing-point lowerings have been derived from their accurately known heats of fusion; thus for water 1.859° . But for most solvents they have been obtained by the direct inductive method; thus for benzene 5.075° (*Batson and Kraus, 1934*).

Prob. 24. — Molal Freezing-Point Lowering Evaluated. —

a. Find the molal freezing-point lowering for water from the following data obtained with solutions of mannite $C_6H_{14}O_6$ (*Flügel, 1912*):

Weight-Molality	0.01041	0.0204	0.0506	0.0957
Freezing-Point	-0.0193	-0.0379	-0.0946	-0.1790

b. When 1 g. of ice melts at 0° , the heat absorbed is 79.7 cal. Find the molal freezing-point lowering for water.

17. Molecular State of Dissolved Substances Determined by Their Effect on Freezing-Point. — Freezing-point measurements, like those of boiling-point and vapor-pressure, can be used for determining the molecular state of substances in solution; and, because of their convenience, such measurements have been extensively used by chemists, especially for finding the molecular weight of new organic substances. The principles involved and the kind of chemical problems that can thus be solved resemble those discussed in connection with boiling-point, so that only a few types of applications of the freezing-point method are here presented.

Prob. 25. — Molecular Formula of a Dissolved Metal. —

Lead fuses at 327° and has an atomic heat of fusion of 1161 cal.

a. Find the molal freezing-point lowering for lead. (Note that the value is much larger than those for non-metallic solvents.)

b. On cooling a melt containing 1.08 g. of silver and 100.00 g. of lead pure lead is known to begin to crystallize out at 315° (under equilibrium conditions). Find the molecular weight of the dissolved silver, and the number of atoms in its molecule. (Compare Prob. 14; IV, 9.)

Prob. 26. — Molecular State Varying with the Nature of the Solvent. — A solution of 0.90 g. of acetic acid ($C_2H_4O_2$) in 50.0 g. of water freezes at -0.558° . A solution of 2.321 g. of acetic acid in 100 g. of benzene freezes 0.970° lower than pure benzene (*Beckmann, 1888*). Calculate the molecular weight of acetic acid in each of these solvents. (Compare Prob. 18; IV, 12.)

Prob. 27. — Polymerization of Alcohol Molecules in Benzene. — Solutions of ethyl alcohol (C_2H_5OH) in benzene show freezing-points as follows: 5.318° at 0.03565 wf.; 5.013° at 0.1074

wf.; 4.618° at 0.2365 wf.; 3.788° at 0.7572 wf.; and 2.768° at 1.922 wf. (*Beckmann, 1888*). Calculate the molecular weight of the alcohol corresponding to each of these pairs of data, using 5.075 as the molal freezing-point lowering of benzene, and taking as its own freezing-point 5.493° (*Richards, Carver, Schumb, 1919*). *Ans.* 49, 52, 63, 103, 165.

Note. — The apparent increase may be due in part to error from using the perfect-solution equation ($T_0 - T = G^0 c$) up to too high molalities; but the large magnitude of the increase indicates extensive association of the alcohol molecules.

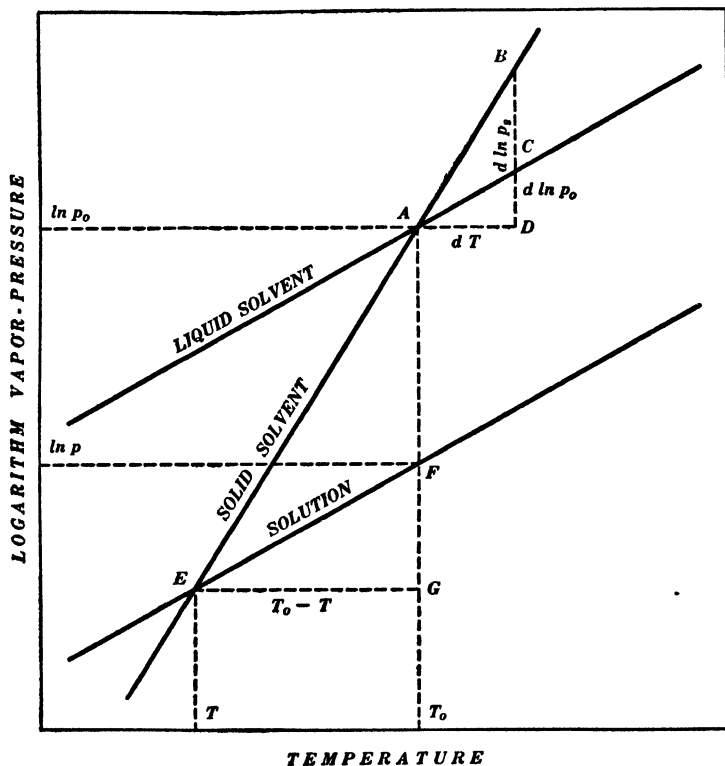
The following statements generalize some of the results as to the molecular state of substances in solution that have been derived from vapor-pressures, boiling-points, and freezing-points. The molecular weights of most substances, other than those that undergo ionization, have been found by boiling-point and freezing-point methods to be the same in the dissolved state as in the gaseous state. This is not true, however, of organic hydroxyl compounds (such as the alcohols and organic acids) in non-oxygenated solvents (such as benzene or chloroform), in which these substances form double or even more highly associated molecules. This indicates that the molecules of hydroxyl compounds are associated also in the state of pure liquids. Oxygenated solvents (such as water, alcohols, acetic acid, ether, esters, acetone) have the power of breaking down these associated molecules into the simple ones; and in such solvents nearly all organic substances have the same molecular weight as in the gaseous state (summary, *Saxton, I. C. T.*, 3, 324; 1928).

A phenomenon which can not be adequately studied by vapor-pressure, boiling-point, or freezing-point methods is *solvation* (*hydration* in the case of water); that is, the extent to which in the solution the solute combines chemically with the solvent, for example, the extent to which alcohol combines with water to form $C_2H_5OH.H_2O$ or $C_2H_5OH.xH_2O$, or sodium with mercury to form $NaHg_{10}$ or other compounds. For, although this removes solvent molecules, and thus decreases the quantity N_0 in the perfect-solution equations (Eqs. 13, 20, 34), yet its fractional decrease is in dilute solutions so small as to be comparable with the experimental errors, and in more concentrated solutions is of a magnitude that may be comparable with the theoretical deviations of those equations arising from other (physical) causes.

Hence, although large solvation may be *indicated* by unusually rapid increase of the calculated molecular effect of the solute, yet (as with mercury and sodium in Prob. 14; IV, 9), it can not be quantitatively determined by molecular-weight methods, as has been wrongly assumed by some investigators.

18. Freezing-Point Lowering of Dilute Solutions Derived from the Vapor-Pressures. — Fig. 3 shows the general relations between the freezing-points T and T_0 of the solution and solvent,

FIGURE 3. VAPOR-PRESSURE-TEMPERATURE DIAGRAM FOR FREEZING-POINTS.



respectively, and the vapor-pressures p , p_0 , and p_s of the solution, liquid solvent, and solid solvent, respectively, at the freezing-point T_0 of the solvent.

In this freezing-point diagram the natural logarithms of the vapor-pressure are plotted as ordinates, and the absolute temperatures as abscissas; natural logarithms being preferred to the pressures themselves, here as in the boiling-point diagram (Fig. 2), because the vapor-pressure-temperature graphs then become substantially straight lines through the temperature-interval that is involved even up to fairly high solute-mol-fractions. The figure is otherwise self-explanatory. It evidently embodies the principle that the liquid solvent and the solution freeze at the temperatures at which their respective vapor-pressures become equal to the vapor-pressure of the solid solvent — hence at the temperature values at which the vapor-pressure curves of the solvent or solution intersect those of the solid solvent.

The geometrical relations of Fig. 3, namely, the similarities of the triangles EAF and ABC, and of the triangles EFG and ACD lead to the conclusion that $AF : EG = BC : AD$; and therefore that:

$$\frac{\ln(p_0/p)}{T_0 - T} = \frac{d \ln p_s}{dT} - \frac{d \ln p_0}{dT}. \quad (36)$$

Replacing the two derivatives in this equation by the expressions given for them by Clapeyron's equations for the molar heat of sublimation $\Delta \tilde{H}_0^s$ for the solid solvent and for the molar heat of vaporization $\Delta \tilde{H}_0^v$ for the liquid solvent, and noting that the molar heat of fusion $\Delta \tilde{H}_0^f$ of the solid solvent equals the difference between these two heats, there is obtained the following relation between the vapor-pressures of solvent and solution and the lowering of the freezing-point, in terms of the heat of fusion:

$$\frac{\ln(p_0/p)}{T_0 - T} = \frac{\Delta \tilde{H}_0^s - \Delta \tilde{H}_0^v}{R T_0^2} = \frac{\Delta \tilde{H}_0^f}{R T_0^2}. \quad (37)$$

By replacing p_0/p by $1/X_0$ in accord with Raoult's law, writing the logarithm as $-\ln(1-X)$, developing it in a series, neglecting the higher terms, and substituting N/N_0 for X , the following expressions are obtained, the second of which is identical with that previously cited (Eq. 34) as expressing the law of freezing-point lowering for perfect solutions:

$$T_0 - T = \frac{R T_0^2}{\Delta \tilde{H}_0^f} X \quad (38); \quad T_0 - T = \frac{R T_0^2}{\Delta \tilde{H}_0^f} \frac{N}{N_0}. \quad (39)$$

**** 19. Analytic Derivation of the Freezing-Point Equations for Solutions Conforming to Raoult's Law.** — The freezing-point-lowering equations can be derived by an analytic method analogous to that used for obtaining the boiling-point-raising equations (IV, 13). This involves the use of partial-derivative expressions of the principles:

- (1) The solvent-vapor-pressure p of a solution is fully determined by its solute-mol-fraction X and by its temperature T (Eq. 24; IV, 13).
- (2) At its freezing-point T this vapor-pressure p is equal to the vapor-pressure p_s of the solid solvent.
- (3) Raoult's law.
- (4) Clapeyron's equation.

This method leads to the following differential equations:

$$-dT = -\frac{R T^2}{\Delta \tilde{H}_x^f} d \ln p. \quad (40)$$

$$-dT = -\frac{R T^2}{\Delta \tilde{H}_0^f} d \ln (1-X). \quad (41)$$

Prob. 28. — Analytic Derivation of the Freezing-Point Equations. — *a.* Derive from principles (1) and (2) stated in the text a general relation between the freezing-point lowering $-dT$ and solute-mol-fraction increment dX , expressed in terms of the three partial derivatives involved. *b.* Modify this relation by replacing the partial derivatives by expressions for them given by Raoult's law and the corresponding Clapeyron equations. *c.* Simplify this result by using again the principle that the two vapor-pressures p and p_s are equal and by using Raoult's law in its finite form, so as to derive Eq. 41. *d.* By integrating this, considering $\Delta \tilde{H}_0^f$ to be constant between the freezing-points T_0 and T of the solvent and solution, obtain Eq. 35.

20. Solutions Conforming to Raoult's Law up to High Concentrations. — Expressions have been derived (Eqs. 29, 31, 35, 41) which make it possible to evaluate the boiling-points and freezing-points, not only of dilute solutions, but also of such concentrated solutions as conform to Raoult's vapor-pressure law. Certain other properties of such solutions are also comparatively simple. Of especial importance are therefore rules or criteria by which predictions can be made as to what kinds of substances form, or are likely to form, Raoult-law solutions.

Conformity with Raoult's law is most directly determined, of course, by vapor-pressure measurements; but it can be tested also by applying the appropriate equations (Eqs. 32 and 35) to boiling-point or freezing-point results. Some of the generalizations to which these methods have led are the following. By measurements of the vapor-pressures of mixtures with two volatile components Raoult-law solutions have been shown to be formed by successive homologues (thus, by benzene and toluene, phenol and cresol, methyl alcohol and ethyl alcohol, methyl acetate and ethyl acetate, ethylene and propylene bromides); also by corresponding compounds of the different halogens (such as ethyl bromide and iodide, or chlorobenzene and bromobenzene) at all concentrations. Such solutions have also been proved by freezing-point-composition measurements throughout the whole range of concentration to be produced by another important group of organic substances, namely, by the isomeric di-substituted benzenes (thus, by ortho, meta, and para dinitrobenzenes or nitroanilines) (*Johnston, Andrews, Kohman, 1925*).

Prob. 29. — Graphic Representation of the Freezing-Points of Solutions Conforming to Raoult's Law. — a. Referring to Eq. 41, state the functions of the freezing-point and of the solvent-mol-fraction which when plotted against each other give a straight-line graph in case the solutions conform to Raoult's law and in case the heat of fusion be considered constant. *b.* The two metals zinc and cadmium form liquid solutions conforming roughly to Raoult's law up to moderate cadmium concentrations, and the solid phase separating may be considered to be pure zinc. The freezing-points of zinc and of solutions of cadmium in zinc are:

Atom-Percent Cd	0	0.58	1.46	3.08	8.76	10.28
Freezing-Point	418.5	415.8	411.7	404.3	381.8	375.0°C

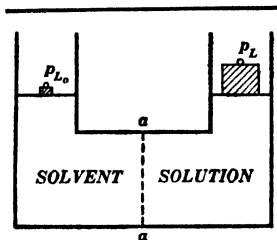
Plot these data on a large-scale diagram in the way considered in *a*, and draw a representative line through the points. *c.* Draw also on the diagram a line representing the freezing-points of solutions that conform to Raoult's law, taking the atomic heat of fusion of zinc as 1670 cal.

Prob. 30. — Analysis of Concentrated Solutions Conforming to Raoult's Law by Freezing-Point Measurements. — A sample of benzene (C_6H_6) containing toluene ($C_6H_5CH_3$) is found to begin to freeze (when overcooling is avoided) at -4.03° . These two substances form solutions that conform to Raoult's law. Pure benzene freezes at $+5.49^\circ$, and has a molar heat of fusion of 2368 cal. Find the percentage by weight of toluene in the sample.
Ans. 16.2%.

V. OSMOTIC PRESSURE OF SOLUTIONS.

21. Osmotic Pressure in General. — When a solution is separated from a pure solvent, as illustrated in Fig. 4, by a wall

FIGURE 4.
OSMOTIC PRESSURE.



aa which allows this solvent to pass through it, but prevents entirely the passage of the solute, the solvent is drawn through the wall into the solution. This flow of solvent may, however, be prevented by applying a pressure p_L to the solution greater by a definite amount than the pressure p_{L_0} upon the pure solvent; and the solvent may be forced out of the solution by exerting a still greater pressure upon the solution. The

pressure-difference (obtained by subtracting from the pressure applied to the solution that applied to the pure solvent) which produces a condition of equilibrium such that there is no tendency for the solvent-substance to flow in either direction is called the *osmotic pressure* P of the solution. That is:

$$P = p_L - p_{L_0}. \quad (42)$$

This pressure-difference may be produced either by applying a (positive) pressure to the solution or a negative pressure (a suction) to the solvent. The magnitudes of these two varieties of osmotic pressure do not differ substantially except at very high values. Compression of the solution is much more readily realized in practice, and is used in experimental measurements. Stretching the solvent by exerting suction upon it has the advantage of greater simplicity in deriving rigorous relations, since it involves the compressibility of the solvent, instead of that of the solution; and it will be employed for this purpose below. This operation is not merely hypothetical; for liquids have in fact been subjected to negative pressures of many atmospheres, without the column breaking, and their compression-coefficients under such pressures have been measured and found to show no discontinuity in passing through zero pressure (*Worthington, 1892*).

Walls of the kind above described are known as *semi-permeable walls* (III, 7). Certain animal membranes, such as

parchment or bladder, are permeable for water, but not for certain solutes of high molecular weight or for substances whose molecules are clustered into large aggregates (the so-called *colloids*). The walls encasing some plant and animal cells are also very perfect semipermeable walls for solutions of such substances. Osmotic pressure therefore plays a highly important role in the physiological processes of plants and animals.

Artificial semipermeable walls that retain completely substances like cane-sugar ($C_{12}H_{22}O_{11}$) were first made (*Pfeffer, 1877*), by precipitating cupric ferrocyanide or other gelatinous substance within the pores of an unglazed porcelain cell, which gives the precipitate sufficient rigidity to withstand high pressures. Such a cell is filled with the solution, which is then brought into direct contact above with a mercury column which serves to measure the pressure that develops when the cell is immersed in pure water under atmospheric pressure. As a result of elaborate investigations (*Morse, Frazer, Holland, 1899–1913; Berkley, Hartley, 1909, 1919*) the mechanical difficulties were finally overcome; and reliable measurements of the osmotic pressure of aqueous solutions of cane-sugar were made up to 273 atmospheres.

In chemical principles osmotic pressure serves (like vapor-pressure) to correlate thermodynamically various properties of solutions; and in fact such correlation was first fully attained with its aid (*van't Hoff, 1886*). The correspondence between the laws of osmotic pressure and gaseous pressure at small concentrations enables, moreover, perfect solutions and perfect gases to be treated in a closely analogous manner. In this book, where Raoult's law has been adopted as the basis of the thermodynamic treatment of the properties of solutions, the laws of osmotic pressure will be theoretically derived from that law (*IV, 23–25*).

22. Laws of the Osmotic Pressure of Perfect Solutions. Relations to Temperature and Molar Composition. — Direct measurements of osmotic pressure made with the aid of semipermeable walls (*IV, 21*), as well as its theoretical relationships to vapor-pressure considered below, have shown (*van't Hoff, 1886*) that, as the concentration of the solute approaches zero, the osmotic pressure of solutions conforms to *perfect-solution laws* identical in form with those to which the pressure of perfect gases

conforms. Namely, at absolute temperature T for a perfect solution containing N mols of solute present in a volume v of the solution or associated with the (substantially equal) volume v_0 of the solvent, or for a perfect solute at volume-molal concentration c_v or c_{v_0} (IV, 1), the osmotic pressure P is expressed by the following equations, in which R is the gas-constant:

$$P v = N R T, \text{ or } P = c_v R T. \quad (43)$$

$$P v_0 = N R T, \text{ or } P = c_{v_0} R T. \quad (43a)$$

This shows that a solute in perfect solution produces an osmotic pressure equal to the pressure which the same chemical species would exert at the same temperature if it were a perfect gas having the same volume as the solution or as the solvent.

Prob. 31. — Osmotic Pressure Evaluated by the Perfect-Solution Laws, and Its Relation to Hydrostatic Pressure. — a. Calculate the osmotic pressure at 27° of a 4.40% solution of glucose ($C_6H_{12}O_6$) in water. *b.* Find the height of a column of the solution (whose density is 1.015 g./ml.) which would balance this osmotic pressure, if the column of solution were separated from pure water at 27° by a semipermeable wall.

Table V illustrates the remarkable precision with which osmotic pressure has been measured in a few cases, and shows that the conformity of the results (*Morse, Frazer, Holland, 1914*) with the perfect-solution equation $P = (N/v_0) R T$ is close in the case of mannite even up to 0.6 wm. and of sucrose at 0.1 wm., but that the percentage differences (referred to the calculated value) increase rapidly in the case of sucrose.

TABLE V. OSMOTIC PRESSURES IN ATMOSPHERES OF AQUEOUS MANNITE AND SUCROSE SOLUTIONS AT 40° .

Weight-Molality c	Observed		Calculated	Percent Difference	
	Mannite	Sucrose	$P = (N/v_0) R T$	Mannite	Sucrose
0.1	2.557	2.560	2.549	+0.27	+0.43
0.2	5.107	5.163	5.099	+0.14	+1.24
0.4	10.216	10.599	10.198	+0.18	+3.93
0.6	15.315	16.146	15.299	+0.16	+5.53
0.8	—	21.806	20.398	—	+6.90
1.0	—	27.701	25.497	—	+8.65

23. Reversible Osmotic Processes of Diluting Solutions.

— Fundamentally, the great theoretical significance of the discovery of methods of quantitative measurement of osmotic pressure arises from the fact that there was thereby discovered a new mechanical device by which a solvent can be removed from or added to a solution by a thermodynamically reversible process; for the realization in principle of a reversible process of bringing about a new type of phenomenon is always the first step in its treatment by the second law of thermodynamics.

The possibility of making osmotic processes reversible will therefore be illustrated. If the solvent be simply poured into the solution, there would be produced no work (other than that corresponding to the small volume-change); yet to separate the solvent from the solution considerable work would have to be expended. With the help of an osmotic arrangement like that of Fig. 4, however, the mixing can be carried out reversibly. For this purpose consider a system consisting of one formular weight of pure liquid solvent at pressure p_L of volume $\tilde{v}_0$, and of an infinite quantity of some definite solution in that solvent at the same pressure p_L , both at temperature T . Consider that a mixture of these two liquids at T and p_L is produced as follows:

(1) Expand the formular weight of solvent reversibly under a piston on which there is applied a pressure progressively varied from p_L to p_{L_0} , the latter being the pressure on the solvent at which there is osmotic equilibrium with the solution at pressure p_L .

(2) Place the expanded solvent in contact with the infinite volume of solution through the semipermeable wall, increase the pressure on the solvent by an infinitesimal amount, and cause it to enter the solution, thereby correspondingly increasing its volume under the constant pressure p_L .

The free-energy decrease in the first step is the integral of $-\tilde{v}_0 dp$ from p_L to p_{L_0} ; and that in the second constant-pressure step is zero. Neglecting the small change in the volume of the solvent produced by the change in pressure, and noting that $p_L - p_{L_0}$ is the osmotic pressure P , the free-energy decrease attending the mixing of one formular weight of a pure solvent (of volume $\tilde{v}_0$) with an infinite volume of a solution at the same temperature and pressure is seen to be given by the expressions:

$$-\Delta F = \tilde{v}_0 (p_L - p_{L_0}) = P \tilde{v}_0. \quad (44)$$

24. Osmotic Pressure in Relation to Vapor-Pressure and to Molar Composition. — Through free-energy considerations there can be readily derived a relation, closely approximate except at very high concentrations, between the osmotic pressure of a solution at temperature T and the solvent-vapor-pressures p and p_0 of that solution and of the pure solvent.

This may be done in the following way. For the free-energy decrease attending the isothermal mixing of one formular weight of solvent of volume $\tilde{v}_0$ with an infinite volume of solution of osmotic pressure P at pressure p_L , which may now be considered to be equal to its own vapor-pressure p , there has already been derived (Eq. 44; IV, 23) the closely approximate expression $-\Delta F = P \tilde{v}_0$. This same change in state* can, however, be brought about reversibly by the following isothermal vaporization process:

(1) Vaporize the solvent at a pressure equal to its vapor-pressure p_0 .

(2) Expand the vapor from pressure p_0 to pressure p (at its variable molar volume $\tilde{v}$).

(3) Condense the vapor into the solution at the pressure p , equal to its vapor-pressure.

The free-energy decrease attending this process is evidently:

$$-\Delta F = \int_{p_0}^p \tilde{v} dp = (\text{for a perfect gas}) R T \ln \frac{p_0}{p}. \quad (45)$$

Equating these expressions for $-\Delta F$ (Eqs. 44, 45) there results:

$$P = \frac{R T}{\tilde{v}_0} \ln \frac{p_0}{p}. \quad (46)$$

The approximations involved in the derivation of this equation are insignificant except at very high pressures. They are those arising from the assumptions that the vapor conforms between p and p_0 to the perfect-gas equation, and that the volume $\tilde{v}_0$ of the liquid solvent does not vary appreciably with the pressure up to values not exceeding the osmotic pressure. The errors

* The change in state is not *strictly* the same in the two cases, since for simplicity in deriving Eq. 44 the solvent was assumed to be under the same pressure p as the solution. However, the assumption that the solvent originally is at p_0 modifies Eq. 44 only so that it reads $-\Delta F = (P + p_0 - p) \tilde{v}_0$; and the $p_0 - p$ correction is almost always entirely negligible in comparison with P (Prob. 34).

introduced by these approximations are so small that this equation is exact within one percent for any kind of solution, provided its osmotic pressure does not exceed about 100 atmospheres and provided the vapor-pressures do not exceed a few atmospheres.

Prob. 32. — Osmotic Pressure Evaluated from Vapor-Pressure Data. — Calculate the osmotic pressure at 100° of a solution consisting of 29 g. of NaCl and 100 g. of water from its vapor-pressure, 622 mm., and from the specific volume of water, which is 1.043 ml. at 100°. *Ans.* 326 atm.

For a solution that conforms to Raoult's law, according to which $p_0/p = 1 + (N/N_0)$, this equation leads to the following relation between the osmotic pressure and the mol-ratio of the solution:

$$P = \frac{R T}{\tilde{v}_0} \ln \left(1 + \frac{N}{N_0} \right). \quad (47)$$

For dilute solutions, with small mol-ratios, by replacing the logarithm by a series and neglecting its higher terms, the following equations are obtained:

$$P = \frac{N R T}{N_0 \tilde{v}_0} = \frac{N}{v_0} R T; \quad \text{or} \quad P = c_v R T.$$

Since $N_0 \tilde{v}_0$, equal to the volume v_0 of the solvent associated with N mols of solute, approaches the volume v of the solution as the molal concentration approaches zero, these equations may be written for perfect solutions:

$$P v = N R T; \quad \text{or} \quad P = c_v R T.$$

These four equations are seen to be identical with the above-given expressions (Eqs. 43a and 43) of the laws derived from measurements of the osmotic pressure of dilute solutions.

**** 25. More Exact Relation between Osmotic Pressure and the Vapor-Pressures.**—By taking account of the compression-coefficient β (Prob. 6; I, 13) of the solvent (or solution) and of a vapor-pressure lowering correction there can be derived a relation between osmotic pressure and the vapor-pressures of the solvent and solution which is substantially exact even at the highest concentrations. This is true of the following expression, in whose derivation are neglected only second-order corrections.

$$(P + \frac{1}{2}\beta P^2 + p_0 - p) \tilde{v}_0 = \int_p^{p_0} \tilde{v} dp. \quad (48)$$

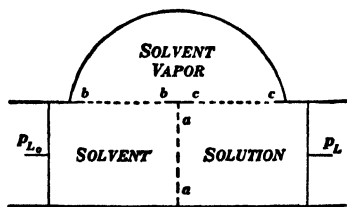
$$= (\text{for a perfect gas}) RT \ln \frac{p_0}{p}. \quad (49)$$

**** Prob. 33. — Derivation of the More Exact Relation between Osmotic Pressure and Vapor-Pressures.** — In analogy with the derivation of Eqs. 44 and 46 derive a more exact relation (Eq. 48) between the osmotic pressure P of a solution, its vapor-pressure p , and the vapor-pressure p_0 of the solvent at any temperature T . Take into account, in finding the free-energy decrease in terms of osmotic pressure, that (1) the initial pressure on the solvent must be p_0 (not p as in Eq. 44), and that (2) the formular volume $\tilde{v}_0'$ of the liquid solvent varies with the pressure P in accord with the equation $\tilde{v}_0' = \tilde{v}_0 (1 - \beta P)$, where β is a (constant) compression-coefficient and $\tilde{v}_0$ is the formular volume at zero pressure. Neglect terms that are products of two small quantities.

**** Prob. 34. — Corrections for the Compressibility of the Solvent and for the Vapor-Pressure Difference of Solvent and Solution.** — *a.* The compression-coefficient β of water at 100° is 0.000043 per atm. Calculate the osmotic pressure of the aqueous NaCl solution of Prob. 32, taking account of this compressibility; and find the percentage effect of this compression correction. *b.* From the data of Prob. 32 find the percentage effect of correcting the osmotic pressure P by the term $p_0 - p$.

26. The Vapor Equilibrium in Relation to the Osmotic Equilibrium. Effect of Pressure on the Vapor-Pressure of Liquids. — In an osmotic arrangement like Fig. 4, when the applied pressures p_{L_0} and p_L are such that there is osmotic equilibrium and therefore no tendency for the solvent to pass through the semipermeable wall, it follows from the perpetual-motion principle that the vapor-pressure of the pure solvent must equal its vapor-pressure in the solution. This is illustrated by Fig. 5,

FIGURE 5. OSMOTIC AND VAPOR EQUILIBRIA.



in which the vapor of the solvent is in contact both with the liquid solvent and with the solution through walls bb and cc permeable only to the solvent vapor, and in which the two liquid phases are separated by a wall aa permeable for the liquid solvent, but not for the solute. This equality of the vapor-pressures is brought about by the difference in the pressures applied to the solvent and to the solution; for the vapor-pressure of any liquid is increased by increasing the pressure upon it. Thus the larger pressure p_L on the solution increases its vapor-pressure p so that it becomes equal to the vapor-pressure p_0 of the pure solvent under the smaller applied pressure p_{L_0} .

**** Effect of Pressure on Vapor-Pressure Derived.**

Consider an apparatus that consists of a horizontal cylinder containing one mol of a liquid and an infinitesimal quantity of its vapor separated by a vertical wall permeable only for the vapor, and closed by pistons against the vapor and liquid on which the equilibrium pressures p and p_L are applied. Consider that two different isothermal reversible processes are carried out by which at T the one mol of liquid in the state p_L and $\tilde{v}_L$ is changed to its vapor in the state $p + dp$ and $\tilde{v} + d\tilde{v}$, as follows:

(1) In one process first force the liquid under the constant pressure p_L through the semipermeable wall, producing vapor under the equilibrium pressure p of volume $\tilde{v}$; and then compress this vapor (with the wall closed) to the state $p + dp$ and $\tilde{v} + d\tilde{v}$.

(2) In the other process first compress the liquid (with the wall closed) into the state $p_L + dp_L$ and $\tilde{v}_L + d\tilde{v}_L$; and then force this liquid under the constant pressure $p_L + dp_L$ through the (reopened) wall, producing vapor at the equilibrium pressure $p + dp$ and at volume $\tilde{v} + d\tilde{v}$.

The free-energy decreases attending these processes are $-\tilde{v} dp$ and $-\tilde{v}_L dp_L$, respectively. From this it is seen at once that the increment dp in vapor-pressure caused by an increment dp_L in the pressure applied to the liquid is given by the expressions:

$$\tilde{v} dp = \tilde{v}_L dp_L; \text{ or } \frac{dp}{dp_L} = \frac{\tilde{v}_L}{\tilde{v}}. \quad (50)$$

Integrating these expressions from the pressure value p_0 in each case to the pressure values p and p_L under the approximate assumptions that the vapor obeys the perfect-gas laws and that the (slightly compressible) liquid undergoes no change in its volume $\tilde{v}_L$, the following expression for the effect of a pressure p_L on the vapor-pressure p_0 results:

$$R T \ln \frac{p}{p_0} = \tilde{v}_L (p_L - p_0). \quad (51)$$

Since the perpetual-motion principle shows that the pressure-difference $p_0 - p_L$ which decreases the vapor-pressure p_0 of the solvent so that it equals the vapor-pressure p of a solution is the osmotic pressure P of that solution, there results:

$$P \tilde{v}_L = P \tilde{v}_0 = R T \ln \frac{p_0}{p}.$$

This is the previously obtained relation (Eq. 46) between the osmotic pressure of a solution and the vapor-pressures of the solvent and solution, now obtained by a different method.

Prob. 35. — Derivation of the Effect of Applied Pressure on the Vapor-Pressure of a Liquid. — *a.* Sketch the apparatus described above for carrying out the reversible processes. *b.* Formulate the free-energy decrease attending each step of each of those processes, and derive Eq. 51.

Prob. 36. — Change in Vapor-Pressure of a Liquid with the Pressure. — Calculate the vapor-pressure of water at 100° under a pressure of 50 atm. The specific volume of liquid water at 100° is 1.043 ml./g.

VI. SOLUTE-VAPOR-PRESSURE AND SOLUBILITY OF GASES.

27. Henry's Law of the Vapor-Pressure of Solutes and of the Solubility of Gases. — In addition to Raoult's law, which relates to the vapor-pressure of the solvent, there is another fundamental law of perfect solutions, known as *Henry's law*, which relates to the vapor-pressure of the solute in such solutions. This law states that at any definite temperature the vapor-pressure of any chemical species present in a solution becomes proportional to its mol-fraction as this approaches zero (*Henry, 1803*).

Henry's law may also be expressed in the following form. At any definite temperature the weight-molal concentration of any chemical species in a solution becomes proportional to the pressure of that species in a gas-phase in equilibrium with the solution, as this concentration and this pressure approach zero. The equilibrium concentration c is the weight-molal *solubility* of the chemical species when its pressure in the gas-phase is p . Henry's law is therefore also a law of gas solubility.

Henry's law is expressed by the equations:

$$p = K_x X \quad (52); \quad c = K p. \quad (53)$$

Here K_x and K are *distribution-constants* whose values are determined by the nature of the volatile solute and of the solvent and by the temperature.

The second form of Henry's law is for perfect solutions equivalent to the first form. For, on the one hand, the mol-fraction $N/(N_0 + N)$ as it approaches zero becomes equal to the mol-ratio N/N_0 , and this is proportional to the weight-molality (N/m_0 in kg.) of the solute; and, on the other hand, the vapor-pressure of a substance in a solution is equal to its partial pressure in a gaseous phase that is in equilibrium with that solution.

It is evident that Henry's law still holds for dilute solutions when the solute-concentration is expressed as volume-molality c_v , that is, as the number of mols of solute per liter of solution (N/v); or when it is expressed in terms of the number of mols of solute per liter of solvent (N/v_0). In fact, the solubilities of gases are often recorded in all these ways, as well as in other ways; and the distribution-constant K varies accordingly. In

this book distribution-constants are usually expressed as weight-molalities, so as to secure uniformity with the expression of the equilibrium of chemical reactions.

Henry's law is conformed to more closely as the pressure of the gas and the concentration of the solute approach zero. Like the other laws of perfect solutions, it holds true approximately for dilute solutions; thus within 1 to 2 percent, up to a pressure of one atmosphere and up to a solute-mol-fraction of 0.02. It will be theoretically shown below (IV, 29) that it holds true up to any solute-mol-fraction up to which Raoult's law holds for the solvent-vapor-pressure.

It is to be noted that Henry's law expresses conditions of equilibrium, and that these conditions are often attained between a gaseous and liquid phase only by long-continued intimate contact.

Henry's law, like Raoult's law, relates to the distribution of some definite kind of molecule between the gas phase and the liquid phase. Hence, in applications of it, the same chemical species in the two phases must be considered; and there must be employed: (1) the partial pressure of that species in the gas phase, not the total pressure of the gas; and (2) the concentration of that species in the solution, not that of the chemical substance (component) which may have been taken to yield that species. Thus, consider the distribution of the substance sulfur dioxide between an air-containing gaseous phase and its aqueous solution, in which it exists partly as each of the three species SO_2 , H_2SO_3 , and $\text{HSO}_3^- (+\text{H}^+)$. In this case Henry's law requires, not that the total concentration of solute, but that the concentration of the SO_2 itself be considered, and that this be proportional to the partial pressure of the SO_2 in the gas, not to the total pressure of the gas. This corresponds to the fact that only SO_2 molecules are directly involved in the equilibrium between the liquid and the gas.

When, however, the only change in dissolving a substance is that it partially combines chemically with the solvent, thereby forming a *solvate* (a *hydrate* with water) (IV, 17), then the total concentration may be employed; for the fraction solvated is in dilute solution independent of the concentration of the substance, as will be shown later. Thus, though the substance CO_2 on

dissolving in water is partly converted into the hydrate H_2CO_3 (which is substantially unionized, except at very small concentrations), yet the solubility of carbon dioxide gas, as found by determining the total quantity dissolved, changes with the pressure in accordance with Henry's law.

Since little is known about the degree of solvation, it is customary to consider a partially solvated solute that is unionized (as is carbon dioxide except at very small concentrations) to have a molality equal to its formality, even though this is in reality the sum of the molalities of two or more chemical species (CO_2 and H_2CO_3). According to the relations that may be under discussion the specified molality is arbitrarily attributed either to the unsolvated species (CO_2) or to the solvated species (H_2CO_3); thus in dealing with the solubility of carbon dioxide, the concentration of the species CO_2 in the solution is naturally employed, whereas in considering the ionization of carbonic acid, the concentration of the species H_2CO_3 is commonly used.

28. Applications of Henry's Law. — Since Henry's law is of extraordinary importance in chemical considerations of many kinds, it is illustrated below by a variety of typical problems.

Prob. 37. — Vapor-Pressure of a Solute at Different Concentrations. — A mixture of air and ammonia containing 1 mol-percent of NH_3 is passed at 25° and 1 atm. through water. The saturated solution is found by titration to be 0.553 wf. in NH_4OH . Calculate the partial vapor-pressure of NH_3 in a solution 1.00 wf. at 25° . The vapor-pressure of water at 25° is 23.8 mm.

Prob. 38. — Determination of the Solubility of a Pure Gas in Water. — In a gas buret over mercury 60 ml. of dry carbon dioxide at 25° and 1 atm. are placed, 40 g. of water are introduced, and the gas and water are shaken together at 25° until equilibrium is reached, keeping the pressure on the gas 1 atm. The volume of the (moist) gas is then found to be 28.9 ml. Calculate the weight-formal solubility of carbon dioxide in water at 25° when its partial pressure is 1 atm., neglecting effects that influence the result less than 0.5 %. *Ans.* 0.0338 wf.

Prob. 39. — Experiment Illustrating the Solubility of a Pure Gas in Water. — A dry flask of 1000 ml. capacity is filled with dry hydrogen sulfide gas at 25° and 1 atm., 100 g. of water are forced into it, and the flask is shaken at 25° until equilibrium is reached. The flask is then connected with a manometer, and the pressure is found to be 684 mm. Calculate the weight-molal solubility of H_2S at 1 atm. in water at 25° . *Ans.* 0.102 wm.

Prob. 40. — Concentration of Oxygen, Nitrogen, and Argon in Air-Saturated Water. — 100 g. of water at 20° dissolve 3.11 ml. of oxygen, 1.57 ml. of nitrogen, and 3.36 ml. of argon when the pressure of each gas is 1 atm. *a.* Calculate the corresponding weight-molal solubility of each gas. *b.* Calculate the mol-fraction of each constituent in the gas mixture obtained by shaking water at 20° with air, expelling the dissolved gas by boiling, and drying it. *c.* Tabulate the molar composition of this gas beside that of air (III, 7). *Ans. b, 0.34 for O₂.*

Prob. 41. — Concentration of Carbon Dioxide in Air-Saturated Water. — From the solubility (0.0338 wf.) of carbon dioxide at 1 atm. in water at 25° calculate the weight-formality of CO₂ (in all its forms) in water which has become saturated with the gas by contact, at 25° and 1 atm., with air containing 0.03 mol-percent of CO₂. At the small concentration of this saturated solution 15.0% of the dissolved carbon dioxide is converted into the ions H⁺ and HCO₃⁻.

Prob. 42. — Complex Formation in Solution. — The partial vapor-pressure of NH₃ in an aqueous solution 0.3 wf. in NH₃ and 0.1 wf. in AgNO₃ is at 25° equal to that in a 0.1 wf. solution of NH₃ in water. State and explain the conclusion that can be drawn as to the formula of the complex salt formed, considering all the silver nitrate to be combined with ammonia, and assuming that the distribution-constant of the NH₃ is not affected by the silver salt.

Aside from any chemical action, the presence of a salt in the solution commonly decreases the solubility of a volatile substance at a given pressure in the gas phase; or conversely, it increases its vapor-pressure at a given concentration in the solution. This phenomenon is known as the *salting-out effect*. It is often considerable even in 0.1 wf. salt solutions, and may become very large at high salt concentrations. It varies greatly with the nature of the salt. For example, at 15° a 0.5 vn. KCl solution dissolves 8.8% less CO₂, and a 0.5 vn. HCl solution 2.5% less CO₂, than an equal volume of pure water.

**** 29. Solute-Vapor-Pressure in Relation to Solvent-Vapor-Pressure and to Osmotic Pressure.** — Henry's law of the vapor-pressure of solutes, Raoult's law of the vapor-pressure of solvents, and van't Hoff's laws of osmotic pressure can be thermodynamically derived from one another (*van't Hoff, 1886*). This can be done in the two ways to be now outlined.

There will be derived later a general thermodynamic relation between the changes in the two vapor-pressures p_A and p_B which the (volatile) components of a binary solution respectively undergo when the mol-fraction of each component X_A and X_B (equal to $1 - X_A$) of the solution changes by an infinitesimal amount. This relation, known as *Duhem's equation*, has the following form, in which X_A and X_B denote the mol-fractions (corresponding to the perfect-gas molecular weights) of the components of which the liquid solution consists:

$$X_A \frac{d \ln p_A}{dX_A} = X_B \frac{d \ln p_B}{dX_B}. \quad (54)$$

For a solution with a solute B up to whose mol-fraction X_B Raoult's law holds for the solvent A, the solvent-vapor-pressure p_A equals $X_A p_{A0}$, so that $d \ln p_A = d \ln X_A$, and Duhem's equation (Eq. 54) assumes the following forms, in which K is the indefinite integration-constant:

$$d \ln p_B = \frac{dX_B}{X_B}; \quad \text{or} \quad p_B = K X_B. \quad (55)$$

The last is an expression of Henry's law; and hence it follows that Henry's law holds true for the vapor-pressure of the solute in any solution up to the solute-mol-fraction X_B up to which Raoult's law holds for the vapor-pressure of the solvent.

The relation to osmotic pressure of the vapor-pressure of the solute can also be derived by finding the free-energy decrease attending two ways of bringing about the transfer at T of one mol of a volatile solute; for example, of oxygen, from an infinite quantity of a solution in which its osmotic pressure is P and its vapor-pressure p into an infinite quantity of another solution in which its osmotic pressure is $P + dP$ and its vapor-pressure is $p + dp$. Let the molar volumes of the solute in the two gas phases be $\tilde{v}$ and $\tilde{v} + d\tilde{v}$, and the volumes of the solvent with which one mol of solute is associated in the two solutions be v_0 and $v_0 + dv_0$. Now for bringing about this transfer two reversible processes are available, resembling those previously outlined (IV, 24); namely, an osmotic process and one of isothermal distillation.

Without giving in detail the lengthy formal description of the osmotic process, it may be stated that the free-energy decrease attending it is given by the simple expression $-\Delta F = -v_0 dP$. And a little consideration shows that the free-energy decrease attending the vaporization of the solute out of one solution, the change in volume of the vapor, and its condensation into the other solution is given by $-\Delta F = -\tilde{v} dp$. Equating these two equations there results the following expressions, in the last of which c_{v_0} (equal to $1/v_0$) represents the volume-molality of the solute:

$$v_0 dP = \tilde{v} dp; \quad (56)$$

$$dP / c_{v_0} = R T d \ln p \text{ (when the gas is perfect).} \quad (57)$$

In virtue of van't Hoff's law the osmotic pressure P equals $c_{v_0} R T$. Introducing for dP the corresponding expression $dP = R T dc_{v_0}$, and integrating, there results the following equation, in which K is an undetermined integration-constant:

$$\ln p = \ln c_{v_0} + \ln K; \text{ or } p = K c_{v_0}. \quad (58)$$

This is Henry's law; and the result shows that this law holds up to any solute-concentration c_{v_0} up to which the osmotic-pressure law $P = c_{v_0} R T$ holds. It was in fact, by the converse of this process, namely, by starting with Henry's law, that the laws of osmotic pressure and of the vapor-pressure of the solvent were originally derived (*van't Hoff, 1886*).

VII. DISTRIBUTION OF SOLUTES BETWEEN PHASES.

30. Distribution of a Solute between Two Non-Miscible Solvents. — Another important law of perfect solutions, called the *law of distribution between phases*, or simply the *distribution law*, has been experimentally established as follows. At any definite temperature the ratio of the equilibrium concentrations of the same chemical species *S* present at small concentrations in two non-miscible solvents *A* and *B* is constant, whatever the initial concentrations. That is:

$$c_s^A/c_s^B = K; \text{ or simply, } c^A/c^B = K. \quad (59)$$

In other words, the distribution-ratio c^A/c^B has in perfect solutions a constant value K determined by the nature of the substances *A*, *B*, and *S*, and by the temperature. For example, if iodine is dissolved in carbon bisulfide and the solution is thoroughly shaken with water at 20°, the ratio of the iodine concentrations in the two solvents, provided these are small, is found to be the same, whatever be the quantities of iodine, carbon bisulfide, and water taken.

This law may be generalized so as to apply to the distribution of a definite chemical species between any two kinds of phases. Thus in its general form it includes Henry's law, since the pressure of a gas at any definite temperature is proportional to its gas concentration; that is, since $p = c R T$.

The law of distribution of a solute between liquid phases, like other laws of perfect solutions, is a limiting law which becomes more exact as the concentrations approach zero, but which holds true approximately provided neither of the two concentrations exceeds a moderate value, such as 1 molal.

In considering the distribution of solutes between liquid phases, volume-molal concentration is often expressed in mols per 1000 ml. of solvent, instead of per 1000 ml. of solution.

The law of distribution between liquid phases can be derived for a volatile solute from Henry's law and the perpetual-motion principle. The validity of the so-derived principle could, however, hardly be dependent on the volatility of the solute, since the phenomenon does not involve its vaporization, and since every solute has a vapor-pressure, even though it be too small to measure. The derivation has therefore general significance.

Prob. 43. — Derivation of the Distribution Law. — *a.* Derive the law of the distribution of a volatile solute between two non-miscible solvents from Henry's law and from the thermodynamic law of equilibrium between phases (II, 19). *b.* State why the derivation applies to concentrated solutions that conform to Raoult's law, as well as to perfect solutions.

31. Applications of the Distribution Law. — The distribution law, like Henry's law, is important, not only because of its direct significance, but because of its use in the study of chemical equilibrium. It is therefore illustrated by a variety of applications.

Prob. 44. — Distribution-Ratio Evaluated from Vapor-Pressure Data. — At 25° the vapor-pressure of NH_3 in a solution of 0.1 fwt. of NH_3 in 1000 ml. of chloroform is 33.25 mm., and in a solution of 0.5 fwt. of NH_3 in 1000 ml. of water is 6.65 mm. Find the distribution-ratio of ammonia between water and chloroform.

Prob. 45. — Extraction of Solutes from Aqueous Solutions by Organic Solvents. — The distribution-ratio of an organic acid between water and ether at 20° is 0.4. *a.* A solution of 5 g. of the acid in 100 ml. of water is shaken successively with three 20-ml. portions of (water-saturated) ether. Find the quantity of acid left in the water. *b.* Find the quantity of acid that would have been left in the water if the solution had been shaken once with a 60-ml. portion of ether. *Ans. a,* 1.48; *b,* 2.00.

Prob. 46. — Determination of Complex Salt Formation. — An aqueous solution containing 0.25 NaCl and 0.20 HgCl_2 in one liter of water is shaken with an equal volume of benzene at 25°. The benzene phase is found by analysis to contain 0.0057 HgCl_2 per liter of solvent, but no NaCl. The distribution-ratio of HgCl_2 between water and benzene at 25° is 12.4 at this concentration. *a.* Calculate the total concentration of mercuric chloride in the aqueous phase, and the concentration of the part of it which is combined with the sodium chloride. *b.* The complex salt has been shown by various physico-chemical measurements to be NaHgCl_3 . Tabulate its concentration and the concentrations of the (uncombined) NaCl and HgCl_2 . *Ans. b,* 0.0707 HgCl_2 per liter.

Prob. 47. — Equilibrium between a Vapor-Phase and Two Liquid Phases. — At 25° the distribution-ratio of Br_2 between carbon tetrachloride and water is 29.3; and the pressure of bromine above an aqueous solution 0.05 volume-molal in Br_2 is 50 mm. Assuming that one liter of this solution is shaken with 50 ml. of carbon tetrachloride, calculate the pressure of the bromine over the carbon-tetrachloride phase. (Bromine exists in all three phases only as Br_2 .) *Ans.* 20.3 mm.

Prob. 48. — Solubilities of a Substance in Two Non-Miscible Solvents in Relation to Its Distribution between the Two Solvents. —
a. 0.568 g. of iodine is dissolved in 50 ml. of carbon tetrachloride, this solution is shaken at 25° with 500 ml. of water, and the aqueous layer is found by titration to contain 0.000466 equivalents of iodine. Calculate a value for the distribution-ratio of iodine between the two solvents, in both of which it exists as I_2 molecules.
b. At 25° the solubility of iodine in water is 0.00133 mol per liter of solvent. Calculate the solubility of iodine in carbon tetrachloride at 25° in mols per liter of solvent. *Ans. a,* 86.0; *b,* 0.1144 (observed, 0.119).

**** 32. Lowering by Solutes of the Solubility of One Solvent in Another Solvent.** — Just as the vapor-pressure of any solvent A is lowered by adding a solute S to it, so the solubility $s_{A_0}^B$ of one solvent A, such as water, in another solvent B, such as ether, not miscible with it, is found to be lowered (to some smaller value s_A^B), when to the solvent A is added any solute S, such as sugar or sodium chloride, not soluble in solvent B. This phenomenon is another one which for slightly soluble solvents and small additions of solute is determined solely by the molar composition. The law expressing it for small solute-mol-fractions is represented by the following equation, in which X_s^A denotes the mol-fraction of S in the solution in solvent A:

$$\frac{s_{A_0}^B - s_A^B}{s_{A_0}^B} = X_s^A. \quad (60)$$

Prob. 49. — Lowering of Solvent Solubility Derived from Vapor-Pressure. — At 25° the saturated solution of bromine in water contains 3.45 g. or 0.0216 mol of Br_2 in 1000 g. of water, and the saturated solution of water in bromine contains 0.460 g. or 0.0256 mol of H_2O in 1000 g. of Br_2 . *a.* Find the weight of water dissolved by 1000 g. of bromine, when this is in equilibrium at 25° with a saturated aqueous solution of $Ca(NO_3)_2$, which has a vapor-pressure of 12.0 mm. at 25°, where the vapor-pressure of pure water is 23.8 mm.

Prob. 50. — Lowering of Solvent Solubility Derived from Molar Composition. — Liquid bromine forms with water at 25° a saturated solution containing 0.0216 mols of Br_2 in 1000 g. of water. Find the weight of bromine that would dissolve in 1000 g. of water saturated at 25° with respect to a solution of 3.32 g. of CBr_4 in 80 g. of bromine.

Prob. 51. — Derivation of the Solvent-Solubility Law. — Derive Eq. 60 from Raoult's law and Henry's law.

VIII. DEVIATIONS FROM RAOULT'S LAW AT HIGHER CONCENTRATIONS. PARTIAL VAPOR-PRESSURES IN SOLUTIONS WITH TWO VOLATILE COMPONENTS.

33. Experimental Determination of Partial Vapor-Pressures.—The deviations from Raoult's law and Henry's law at higher concentrations can be most fully and simply studied in the case of two-component systems where both the substances have measurable vapor-pressures. As such systems have much interest also in connection with the practice of fractional distillation, they will be here considered.

A method commonly employed for experimentally determining the partial vapor-pressures of solutions of two or more volatile components consists in distilling off a small fraction from a large volume of the solution of known composition, condensing this distillate, and determining its composition by chemical analysis or by the measurement of some physical property, such as density or refractive index. From this composition and the pressure under which the distillation took place the two partial vapor-pressures are calculated by Dalton's law (III, 7); thus on the (often rather inexact) assumption that the vapors conform to the perfect-gas equation. To determine the vapor-pressures for a series of solutions at a specified temperature the applied pressure is so adjusted that each solution boils at this temperature.

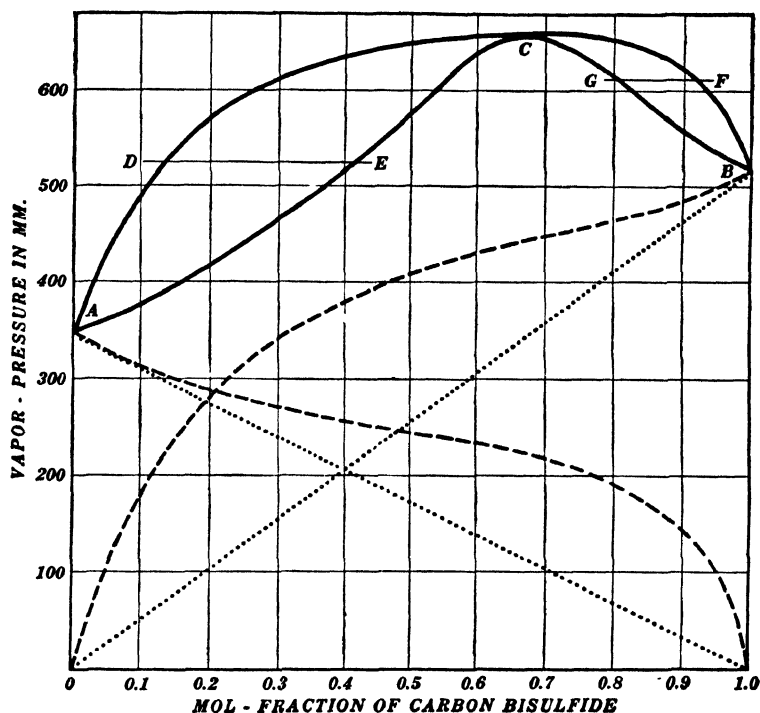
Prob. 52. — Partial Pressure Determined by Distillation. —

From a solution of two volatile substances A and B containing N_A mols of A and N_B mols of B a small fraction is distilled off at the temperature T while a pressure p is exerted upon it. This first portion of distillate is found to consist of N'_A mols of A and N'_B mols of B. Derive an algebraic expression for the partial vapor-pressures p_A and p_B of the two substances in the solution.

34. Vapor-Pressure-Composition Diagrams.—The variation of the vapor-pressures of two-component solutions with their composition is most clearly represented by a *vapor-pressure-composition diagram*, such as that in Fig. 6.

In this diagram, for which the experimental data (Zawidzki, 1900) were obtained by the method described above (IV, 33), there are plotted as ordinates the total and partial

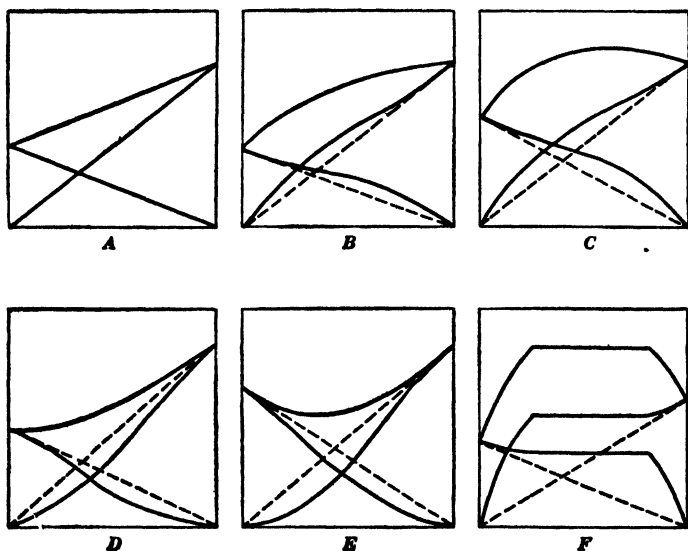
FIGURE 6. VAPOR-PRESSURE-COMPOSITION DIAGRAM FOR ACETONE AND CARBON BISULFIDE AT 31.17°.



vapor-pressures at 35.17° of solutions of acetone and carbon bisulfide, and as abscissas the mol-fractions of carbon bisulfide in the liquid or in the vapor. The uppermost graph is a plot of the total vapor-pressure against the mol-fraction in the liquid. The graph just below it is a plot of the total vapor-pressure against the mol-fraction in the vapor in equilibrium with the solution. Thus, points *E* and *G* represent the composition of the vapor from solutions of the composition and total vapor-pressure given by the points *D* and *F*, respectively. The two broken curves below the solid ones are plots of the partial vapor-pressures (calculated as in Prob. 52) of acetone and carbon bisulfide, respectively, against the composition of the liquid. The dotted straight lines are similarly plots of the partial vapor-pressures that correspond to Raoult's law.

Six of the simplest and most common types of vapor-pressure-composition diagrams are illustrated in Fig. 7. In these diagrams the two lower graphs always represent the two partial vapor-pressures, and the uppermost graph the total vapor-pressure of the solutions. Diagram *A* represents solutions that conform to Raoult's law; diagrams *B* and *C* represent pairs both of whose components have too large vapor-pressures; diagrams *D* and *E* pairs whose components have too small vapor-pressures; and diagrams *C* and *E* represent cases where the divergences are so large and the vapor-pressures of the two pure components so nearly equal that the total vapor-pressure curve shows a maximum or a minimum. A common case, illustrated by diagram *F*, is that where the vapor-pressures of the components are much larger than Raoult's law requires and the mixture (like that of ether and water or of bromine and water) separates into two liquid phases, each with definite composition and definite partial vapor-pressures, throughout a considerable range of total composition of the mixture. The case also occurs, though not commonly, in which a component deviates in opposite directions in different parts of the composition range; thus this is true of solutions of water and pyridine.

FIGURE 7. TYPES OF VAPOR-PRESSURE-COMPOSITION DIAGRAMS.



Prob. 53. — Diagram for a Pair of Incompletely Miscible Liquids. — State what each section of each of the graphs in diagram *F* of Fig. 7 represents.

Although not the aspect here under consideration, it may be noted that vapor-pressure-composition diagrams have important practical applications in predicting the results of fractional distillation at constant temperature.

Prob. 54. — Behavior of Solutions on Distillation Predicted from a Vapor-Pressure-Composition Diagram. — *a.* Using Fig. 6, predict the composition of the first portion of the distillate from a solution containing 20 mol-percent of carbon bisulfide and 80 mol-percent of acetone. *b.* Find the composition of the first portion of distillate that would result if this portion were redistilled. *c.* State toward what limiting composition the distillate would tend if the first portions obtained were successively redistilled. *d.* State what would happen if a solution of the composition represented by the point *C* were distilled.

35. Magnitudes of Deviations from Raoult's Law. — Some pairs of substances are found to form solutions both of whose components conform closely to Raoult's law throughout the whole range of composition. In such solutions, which are sometimes called *ideal solutions*, the partial vapor-pressure of each component is equal to the product of its mol-fraction in the solution by its vapor-pressure in the pure (liquid) state, whatever be the proportion in which the components are present. That is, for two components A and B:

$$p_A = p_{A_0} X_A; \text{ and } p_B = p_{B_0} X_B. \quad (61)$$

Some of the typical pairs of substances which conform to Raoult's law at all concentrations have already been specified (IV, 20). Thus this conformity was stated to be close for pairs of successive homologues, such as ethylene and propylene bromides, pairs of compounds of the same organic radical with different halogens, such as ethyl bromide and iodide or chlorobenzene and bromobenzene, and pairs of ortho and meta, ortho and para, and meta and para disubstituted benzenes. It is also true of pairs of some apparently rather dissimilar substances, like benzene and ethylene chloride.

Most pairs of substances, however, are found to form solutions with partial vapor-pressures which diverge markedly,

TABLE VI. DEVIATIONS FROM RAULT'S LAW. VOLUME AND HEAT EFFECTS ON MIXING.

Pair No.	Components	p_{A0}, p_{B0} in mm.	Temperature	$100X_A$	$\frac{p_A}{p_{A0} \cdot X_A}$	$\frac{p_B}{p_{B0} \cdot X_B}$	Volume Increase in ml./mol	Heat Evolved in cal./mol
1	A: $C_2H_5Br_2$ B: $C_3H_5Br_2$	171 127	85°	0-100	1.00	1.00	—	—
2	A: C_2H_6 B: $C_3H_5Cl_2$	266 236	50	0-100	1.00	1.00	—	—
3	A: CH_3OH B: C_2H_5OH	94 44	20	0-100	1.00*	—	+0.0049 .0156 .0161	+3.3 3.7 2.5
4	A: C_2H_6 B: $C_2H_5CH_3$	76 24	20	25 50 75	1.06* 1.06* 1.07*	—	+0.0504 .0816 .0660	-13.7 -18.8 -14.2
5	A: C_2H_6 B: CCl_4	266 309	50	25 50 75	1.07 1.05 1.02	1.00 1.03 1.07	+0.284 .487 .427	-18.1 -26.5 -22.1
6	A: C_2H_6 B: CS_2	95 361	25	25 50 75	1.28 1.14 1.03	1.03 1.09 1.21	+0.572 .731 .527	-111. -146. -106.
7	A: C_2H_6 B: CH_3CO_2H	266 56	50	25 50 75	1.67 1.30 1.11	1.05 1.17 1.72	+0.645 .994 .449	-78. -94. -66.
8	A: $(CH_3)_2CO$ B: CS_2	345 513	35.2	25 50 75	2.32 1.39 1.08	1.18 1.57 2.40	+0.651 .910 .695	-277. -333. -246.
9	A: $(C_2H_5)_2O$ B: $CHCl_3$	397 143	17	25 50 75	0.465 0.720 0.930	0.913 0.700 0.503	-1.08 -1.66 -1.37	+449. 610. 444.
10	A: $(CH_3)_2CO$ B: $CHCl_3$	345 293	35.2	25 50 75	0.605 0.815 0.956	0.932 0.779 0.655	-0.135 -0.151 -0.140	+415. 535. 345.

* These starred values are the ratios of the total pressure to that required by Raoult's law.

sometimes very greatly, from the requirements of Raoult's law. Most of these diverge in the direction of too large vapor-pressures, but some of them do so in the direction of too small vapor-pressures. This highly variable divergence is illustrated by Table VI, in which are given the values (mostly, *Zawidzki, 1900*) of $p_A/p_{A_0} X_A$ and $p_B/p_{B_0} X_B$, quantities which may be called *deviation-coefficients*, and which are unity for any solution conforming to Raoult's law. (The significance of the values in the last two columns in the table will be explained below.)

Inspection of Table VI shows the following facts:

(1) The first and third pairs of substances consisting of successive homologues conform closely to Raoult's law throughout the whole range of composition. The same is true of the second pair C_6H_6 and $C_2H_4Cl_2$. The fourth pair C_6H_6 and $C_6H_5CH_3$, consisting of homologues but with rather different molecules, shows small but appreciable positive deviations. The same is true of the fifth pair C_6H_6 and CCl_4 with dissimilar molecules.

(2) The sixth, seventh, and eighth pairs, consisting of C_6H_6 and CS_2 , C_6H_6 and CH_3CO_2H , and $(CH_3)_2CO$ and CS_2 , thus of very different types of substances, show large positive deviations in the case of both components.

(3) The ninth and tenth pairs, consisting of $(C_2H_5)_2O$ and $CHCl_3$ and of $(CH_3)_2CO$ and $CHCl_3$, again very different types of substances, show large negative deviations.

(4) In the case of all these pairs of substances the vapor-pressures of the two components deviate from Raoult's law in the same direction.

This last conclusion can be shown to be a consequence of Duhem's equation (Eq. 54; IV, 29) in case the deviation-coefficients increase or decrease steadily throughout the whole range of composition, as they do for each of the last five pairs in Table VI.

36. Kinetic-Molecular Interpretations of the Deviations from Raoult's Law. — An expression (Eq. 8; IV, 6; and "Kinetic Interpretation"; IV, 8) has been derived from kinetic considerations for the vapor-pressure p_A of a volatile component A of a solution. This leads to the following equation when applied simultaneously to the vapor-pressures of a solution and of the pure solvent and when the mol-fraction X'_A , equal to $n'_A/(n'_A + n'_S)$,

is introduced into both members:

$$\frac{p'_A}{p_A X'_A} = \frac{\bar{n}'_A (n'_A + n'_B)}{\bar{n}_A n'_A} \cdot \frac{f(\tilde{v}'_A)}{f(\tilde{v}_A)} \cdot e^{-(\dot{x}'_0^2 - \dot{x}_0^2) M/2 R T}. \quad (62)$$

In this equation symbols to which primes are attached represent values prevailing in the solution, and those without primes represent values prevailing in the pure solvent.

Prob. 55. — Kinetic Expression for Raoult's-Law Deviations. — Derive Eq. 62 from Eq. 8 (IV, 6) in the way indicated in the above text.

This expression for the deviation from Raoult's law shows that the deviation depends in a high degree on an exponential function of the quantities $\dot{x}_0$ and $\dot{x}'_0$ which represent the minimum velocities that permit the solvent molecules to escape from the surface of the pure solvent and of the solution, respectively. This minimum velocity increases, however, and the exponential factor containing it decreases in much higher degree, as the attraction of the added solute molecules for the escaping solvent molecules increases. Thus, according as the attraction of B for A is greater or less than that of A for A, the vapor-pressure of A may be expected to be less or greater than Raoult's law requires. In general, molecule attraction must be a highly important factor in determining the deviations from Raoult's law and the types of vapor-pressure-composition diagrams which different pairs of substances yield.

It is doubtless true, to be sure, that the Raoult-law deviation is much affected also by variations in the unknown "collision correction" $f(\tilde{v}_A)$ which represents the fraction of the molecules that reach unit-surface in unit time; but this effect is probably always secondary to that of the variations of the exponential factor. The first factor, expressed as a function of molecule numbers, also influences the Raoult-law deviation, but relatively very slightly.*

* The reciprocal of this factor, in view of the relations $\bar{n}_A = 1/\tilde{v}_A$ and $\bar{n}'_A = 1/\tilde{v}'_A$, can be shown to be equivalent to $X'_A + (\tilde{v}_B/\tilde{v}_A) X'_B$; and this evidently differs from unity only in so far as this is caused by a difference in the molar volumes of the two pure components. This conclusion may be derived from the fact that, if the volume of the solution $\tilde{v}'_A$ (in which one mol of A is present) is considered to be additive, it is given by the expression $\tilde{v}'_A = \tilde{v}_A + \tilde{v}_B n'_B/n'_A$.

Besides these physical effects due to molecule attraction, sometimes called *van der Waals' attraction*, chemical reactions may take place upon mixing the two components. These are mainly of two kinds, as follows:

- (1) Formation of a compound (such as AB , AB_2 , A_2B , etc.).
- (2) Dissociation of one or of both components (thus A_2 into $2A$, B_2 into $2B$, etc.), when polymerized in the pure state.

Chemical combination results in lowering both partial vapor-pressures; and it is difficult to distinguish it from a large *van der Waals' effect*. When, however, maximum effects are observed at a mol-ratio that is the ratio of small whole numbers ($1A$ to $1B$, $2A$ to $1B$, etc.), and when this is true throughout a considerable range of temperature, there is a presumption that a chemical compound forms. This is, of course, also true when the chemical character of the compounds (as in the case of pyridine and acetic acid) is such as to indicate a chemical reaction.

Dissociation of a polymerized compound by dilution, on the contrary, may be expected to cause increase in the partial pressures of that component, since it is the simpler molecule that distributes itself between the liquid and vapor. Thus the effect is like that of diminished molecule attraction.

Prob. 56. — Interpretation of Raoult-Law Deviations by Molecule Attraction. — *a.* State what assumptions have to be made as to the relative attractions of the molecules of A for B and A for A , and of A for B and B for B , in order to account by molecule attraction for the deviations from Raoult's law in the case of each of the last five pairs of components shown in Table VI. *b.* State also which type of diagram shown in Fig. 7 would represent each of these pairs.

Prob. 57. — Interpretation of Raoult-Law Deviations by Compound Formation. — From the vapor-pressure data for the 50 mol-percent solution of the tenth pair of components given in Table VI, assuming arbitrarily that the Raoult-law deviation is wholly due to the formation of a non-volatile compound $(CH_3)_2CO \cdot CHCl_3$, calculate the mol-percent of this compound in the solution, *a*, from the vapor-pressures of the acetone; and *b*, from those of the chloroform.

37. Other Properties Related to Deviations from Raoult's Law. — There will now be considered certain properties of solutions whose values roughly indicate the magnitude of the deviations to be expected between the partial vapor-pressures actually

existing and those required by Raoult's law. It has already been seen that kinetic considerations show that a major factor determining these deviations in case of either component is the difference between the attraction of its own molecules for one another, as shown in the pure state, and the attraction of its molecules for those of the other component in the solution. Properties other than vapor-pressure which are determined by the difference in these attractions are therefore of special significance.

Two such readily measurable properties are: (1) the increase in volume that attends the mixing of the components, when these are both liquid; and (2) the heat-evolution that attends such mixing. For evidently, if no chemical reaction involving change in the nature of the molecules takes place on mixing, a decrease in volume indicates greater, and an increase in volume indicates smaller, molecule attraction in the solutions than in the pure solvent. Similarly, since a volume-increase against an attractive force involves increase in energy-content (as in an imperfect gas; *III*, 32), an absorption of heat on mixing indicates smaller, and an evolution of heat indicates greater, molecule attraction in the solution than in the pure solvent.

Prob. 58. — Approximate Determination of the Heat of Mixing. — Within a vacuum-jacketed glass tube are placed $\frac{1}{2}$ fwt. of acetone ($\text{CH}_3)_2\text{CO}$ and a very thin glass tube containing $\frac{1}{2}$ fwt. of chloroform (CHCl_3); and after equalization of the temperatures the tube containing the chloroform is broken, the mixture stirred, and its temperature measured. In a certain experiment the initial and final temperatures were 0.0° and 20.8° . The specific heat-capacities of acetone and chloroform are 2.10 and 0.976 joules per degree, respectively. Neglecting the loss of heat to the glass apparatus, calculate the calories evolved by the isothermal mixing of the two liquids at the final temperature. (Note that this heat-effect is that for 1 fwt. of the solution.)
Ans. 595 cal.

In Table VI (*IV*, 35) is given a comparison for a variety of solutions of the magnitudes of these physical effects (*Schmidt*, 1926) with the divergences of the partial vapor-pressures from Raoult's law. The table shows, namely, in the last two columns the volume-increase at 17° and the heat-evolution in calories at 13 – 18° which result when 0.25, 0.50, or 0.75 fwt. of one pure liquid component is mixed with 0.75, 0.50, or 0.25 fwt. of the other pure liquid component and the mixture is restored to its

initial temperature. The two preceding columns of the table show, as above described, the ratios of the observed values of the partial vapor-pressures to the values calculated by Raoult's law at the specified temperatures.

It will be seen from Table VI that:

(1) The first four pairs of substances whose vapor-pressures deviate little from Raoult's law show only a relatively small volume-change or heat-effect upon mixing.

(2) Pairs 6, 7, and 8, whose vapor-pressures are much larger than the law requires, are produced out of the components with a relatively large increase of volume and absorption of heat.

(3) Pairs 9 and 10, whose vapor-pressures are much smaller than the law requires, are produced out of the components with a relatively large decrease of volume and evolution of heat.

(4) Increase in volume is accompanied by absorption of heat and decrease in volume by evolution of heat, as molecule attraction seems to require, in all cases except pair 3 where the conditions may well be complicated by depolymerization and compound formation of the alcohols.

The volume and heat effects on mixing afford therefore a fairly reliable indication of the direction and general magnitude of the vapor-pressure deviations that may be expected. It is to be remembered, however, that these effects are composite ones to which the two components contribute somewhat independently, and that compensation may take place. Thus in terms of molecule attraction the attraction of B for A might be less than that of A for A, but greater than that of B for B.

*Thermodynamic Relations between Raoult-Law
Deviations and the Heat-Effects and
Volume-Changes on Mixing.*

It has been shown (Prob. 23; IV, 18) that the molar heats of vaporization of a solvent in the pure state and out of a Raoult-law solution are equal. It follows that the heat absorbed by the mixing of one mol of solvent with an infinite quantity of a Raoult-law solution is zero; for this heat of mixing is equal to the difference in the two heats of vaporization.

This conclusion is derived from Clapeyron's equations and Raoult's law explicitly as follows. By subtracting Clapeyron's equation for the pure solvent from that for the solvent in a solution, and substituting for the difference in the heats of vaporization the heat $\Delta\bar{H}^M$ absorbed by mixing one mol of solvent

with an infinite quantity of the solution there is obtained the equation:

$$\frac{d \ln (p/p_0)}{dT} = \frac{\Delta \tilde{H}^v - \Delta \tilde{H}_0^v}{R T^2} = \frac{\Delta \tilde{H}^m}{R T^2}. \quad (63)$$

Furthermore, Raoult's law requires that the vapor-pressure ratio p/p_0 be determined solely by the composition, thus that it be equal to the mol-fraction X_0 , independently of the temperature. Hence the first member of this equation is equal to zero, and therefore also the second and third members. The heat of mixing is therefore zero for a solution that conforms to Raoult's law through a series of temperatures.

The following thermodynamic expression can by similar considerations be derived for the effect of applied pressure p_L on the vapor-pressure of liquids (Eq. 50; IV, 26):

$$\frac{d \ln (p/p_0)}{dp_L} = \frac{\tilde{v}_L - \tilde{v}_{L0}}{R T}. \quad (64)$$

Here $\tilde{v}_L - \tilde{v}_{L0}$ represents the increase in volume when one mol of solvent (of vapor pressure p_0) and an infinite quantity of a solution (in which the solvent-vapor-pressure is p) are mixed. The equation shows that, only when the volume-change is zero, can the solution conform to Raoult's law, which requires that p/p_0 be constant through a range of applied pressures.

Over the integral volume and heat-content changes previously considered and recorded in Table VI these effects have the theoretical advantages that they are represented by nearly exact thermodynamic equations, and that they refer to the introduction into the solution of the two components separately. But they have the practical disadvantages that they involve quantities, so-called partial molar quantities (IV, 40), that represent the effects attending the mixing of solvent with an infinite volume of the solution, which are seldom known for organic substances and which can be determined only by a laborious process. Furthermore, the partial molar values, when interpreted by the above second-law equations, measure not the Raoult-law deviations themselves, but the effect of temperature or pressure upon them; whereas, interpreted by the first law, the integral quantities afford a direct indication, though not a quantitative one, of the molecule attraction or chemical effects involved.

**** Attraction-Pressure in Relation to Raoult-Law Deviations.**

The internal pressure or attraction-pressure p^A (III, 29) of a liquid affords an approximate quantitative measure of the attraction of its molecules, and is therefore closely related to its

vapor-pressure. To determine this quantity it may be assumed as a reasonable approximation so long as the molecules are at the same distance from one another, as is the case when the volume is kept constant, that a liquid conforms approximately to an equation of state of the following form, analogous to van der Waals' equation but less specialized:

$$(p + p^A)(\tilde{v} - f(\tilde{v})) = RT. \quad (65)$$

In this equation p is the externally manifested pressure, and p^A and $f(\tilde{v})$ are quantities limited only in the respect that they have the same value so long as the volume remains constant.

Differentiation of this equation with respect to temperature at constant volume yields:

$$\left(\frac{\partial p}{\partial T}\right)_{\tilde{v}} = \frac{R}{\tilde{v} - f(\tilde{v})}.$$

From this it follows that:

$$T\left(\frac{\partial p}{\partial T}\right)_{\tilde{v}} = \frac{RT}{\tilde{v} - f(\tilde{v})} = p + p^A; \text{ or } T\left(\frac{\partial p}{\partial T}\right)_{\tilde{v}} = \text{approx. } p^A. \quad (66)$$

The first member of these equations is substantially equal to the attraction-pressure p^A ; for, in the case of liquids at ordinary pressure, the ratio p^A/p is very large.

The value of $(\partial p/\partial T)_{\tilde{v}}$ in the case of pure liquids has in general been most accurately calculated from their thermal expansion-coefficient α and isothermal compression-coefficient β by means of the following equation

$$\left(\frac{\partial p}{\partial T}\right)_{\tilde{v}} = \frac{\alpha}{\beta}. \quad (67)$$

Approximate values of the attraction-pressure can be derived by various other methods (*Hildebrand, "Solubility," 1924*).

The chief use of attraction-pressure with reference to Raoult's law is that the relative values of that pressure for two pure liquid components furnish a fairly reliable indication as to whether they will form solutions that conform to that law at all concentrations; for, in order that they may do so closely, their molecule attractions, and therefore their attraction-pressures, must be substantially equal to one another.

Unfortunately comparatively few accurate data are available for confirming this theoretical conclusion experimentally. The values of the attraction-pressures (*Hildebrand, 1928; I.C.T., 4, 19*) of some components for pairs of which Raoult-law deviations are given in Table VI are however shown in Table VII.

TABLE VII. ATTRACTION-PRESSURES AND RAOULT-LAW DEVIATIONS.

<i>Substances</i>	<i>Attraction-Pressure</i>	<i>Vapor-Pressure Deviation in Equimolar Mixture</i>
<i>A</i> : C_6H_6	4050 atm.	1.06
<i>B</i> : $C_6H_5CH_3$	3780	
<i>A</i> : C_6H_6	4050	1.05
<i>B</i> : CCl_4	3640	1.03
<i>A</i> : C_6H_6	4050	1.14
<i>B</i> : CS_2	5400	1.09
<i>A</i> : $(C_2H_5)_2O$	3100	0.72
<i>B</i> : $CHCl_3$	3830	0.70

It will be seen that the first two pairs in Table VII have components whose attraction-pressures differ by 7 or 10 %, and that this suffices to produce average Raoult-law deviations of 1.06 and 1.04 in the equimolar mixture; also that the last two pairs have components whose attraction-pressures have the ratios 1.33 and 1.24, and that this results in much larger Raoult-law deviations, namely of 1.12 and 0.71 in the equimolar mixture.

IX. ENERGY RELATIONS OF SOLUTIONS.

38. Heat-Content Changes Attending Changes in Volume and Concentration. — By mixing under adiabatic conditions known weights of a solution and of its pure solvent at the same temperature and pressure, noting the change in temperature, and multiplying this temperature-change by the heat-capacity of the mixture, the corresponding heat-content increase ΔH can be experimentally determined. This energy quantity, when referred to that quantity of solution which contains one mol or one formular weight of the solute, is called the *integral molar or formular heat of dilution* $\Delta \tilde{H}_{v_i}^{v_g}$ of the solute between the specified initial and final volumes v_i and v_g .

An important principle as to the value of this quantity has been experimentally established; namely, the principle that, as the concentration of any solution approaches zero, the molar or formular heat of dilution of the solute approaches zero. Hence, the dilution of a perfect solution, like the expansion of a perfect gas, is attended by no change in heat-content. That is:

$$\Delta \tilde{H}_{v_i}^{v_g} = 0, \text{ for perfect solutions.} \quad (68)$$

It can be shown to follow from this equation that the transfer of a solute from a perfect solution of one concentration c_i to one of another concentration c_g is attended by no change in heat-content. That is:

$$\Delta \tilde{H}_{c_i}^{c_g} = 0, \text{ for perfect solutions.} \quad (69)$$

39. Free-Energy Change Attending the Transfer of a Solute between Solutions of Different Concentrations. — The quantity named in this title is of great importance in the thermodynamic and electrochemical treatment of solutions. Expressions for it can be derived in the case of a volatile solute by the following reversible process of isothermal distillation:

(1) Out of an infinite quantity of a solution containing a solute at a concentration c_i or mol-fraction X_i , having a solute-vapor-pressure p_i at temperature T , vaporize one mol of the solute under a constant pressure substantially equal to its own vapor-pressure, producing vapor of volume $\tilde{v}$.

(2) Change the pressure p_i of this vapor reversibly to a pressure p_g which is equal to the partial vapor-pressure at T of the

solute in a second solution containing the solute at a concentration c_2 or mol-fraction X_2 .

(3) Condense the vapor into an infinite quantity of this second solution under a constant pressure substantially equal to its solute-vapor-pressure p_2 .

The changes in free energy in steps (1) and (3) are zero, since the changes in state are at the constant equilibrium-pressures. The total free-energy decrease attending the transfer of one mol of solute is therefore that in step (2); and this is given by the expressions (Eq. 41; II, 17):

$$- \Delta \tilde{F} = \int_{p_2}^{p_1} \tilde{v} dp;$$

or

$$- \Delta \tilde{F} = R T \ln \frac{p_1}{p_2} \text{ (when solute vapor is perfect).} \quad (70)$$

These equations are exact whatever be the concentrations of the solutions. When the concentrations and pressures are so small that the solute conforms to Henry's law, in which case $p_1/p_2 = c_1/c_2 = X_1/X_2$, the molar free energy of transfer of the solute is expressed by the equations:

$$- \Delta \tilde{F} = R T \ln \frac{c_1}{c_2} \text{ (when solute conforms to Henry's law),} \quad (71)$$

$$- \Delta \tilde{F} = R T \ln \frac{X_1}{X_2} \text{ (when solute conforms to Henry's law).} \quad (72)$$

Although these equations were derived by considering a vaporization process in which the solute was assumed to have a small but appreciable vapor-pressure, yet the final expressions relate only to the transfer of a solute from one solution to another, and the result can therefore hardly depend on the volatility of the solute (or solvent). That the equations are indeed applicable to solutes and to solvents of any volatility is shown by the fact that the same result is obtained by considering an osmotic process of transferring the solute from one solution to another, and applying to the result van't Hoff's laws of osmotic pressure, instead of Henry's law of vapor-pressure. This shows that Eqs. 71 and 72 are exact, provided only that the dissolved substance behaves as a perfect solute in the respect that it conforms to the

osmotic-pressure equation, $P = c_v R T$ (Eq. 43; IV, 22), or conforms to the corresponding freezing-point equation, $T_0 - T = X R T_0^2 / \Delta \tilde{H}_f^\circ$ (Eq. 38; IV, 18).

Since Henry's law applies to the concentrations of definite chemical species (IV, 27), it is evident that Eqs. 71 and 72 must be applied separately to the transfer of each species, not to the transfer of the substance as a whole, provided it exists in the solution as two or more different species, as is the case with sulfurous acid or any other partially ionized substance in aqueous solution, or with acetic acid in benzene solution in which it exists as $C_2H_4O_2$ and $(C_2H_4O_2)_2$. Yet, as with Henry's law itself at small concentrations, the formation of a hydrate by the solute, as in the case of CO_2 and H_2CO_3 or of NH_3 and NH_4OH , does not have to be taken into account.

Applications of the Free Energy Equations.

Prob. 59. — Free-Energy Decrease at Large Solute Concentrations. — *a.* Calculate the free-energy decrease in calories attending the transfer at 20° of $1NH_3$ from an infinite quantity of a solution of the composition $1NH_3 \cdot 8\frac{1}{2}H_2O$ in which its vapor-pressure is 80 mm. into an infinite quantity of a solution of the composition $1NH_3 \cdot 21H_2O$ in which its vapor-pressure is 27 mm. *b.* Calculate the free-energy decrease attending the dissolving at 20° of $1NH_3$ at 1 atm. in an infinite quantity of a solution of the composition $1NH_3 \cdot 21H_2O$.

Prob. 60. — Free-Energy Decrease at Small Solute Concentrations. — Calculate the free-energy decrease attending the transfer at 20° of $1NH_3$ from an infinite quantity of 0.1 wf. NH_4OH solution into an infinite quantity of 0.001 wf. NH_4OH solution. The ammonium hydroxide is 1.3% ionized in the 0.1 wf. and 12.5% ionized in the 0.001 wf. solution, and the remaining ammonium hydroxide is y percent dissociated into NH_3 and H_2O in each solution.

Prob. 61. — Evaluation of the Electromotive Force of a Concentration-Cell. — When one faraday ($1 F = 96500$ coulombs) is passed through the following cell the only change in state is the transfer of one equivalent of zinc from the left-hand to the right-hand amalgam:

Zn at c_1 wf. in Hg , $ZnCl_2$ at c wf. in H_2O , Zn at c_2 wf. in Hg .

a. Formulate an expression for the electromotive force E of this cell at T° (II, 19, 24). *b.* Evaluate this electromotive force in volts when at 25° the zinc concentrations in the two amalgams are 0.1 wf. and 0.001 wf. Note that zinc forms monatomic molecules in mercury solution (Prob. 14; IV, 9).

40. Concept of Partial Molar Quantities. — In the thermodynamic treatment of solutions it is convenient to make use of a new concept, which will be now described. Namely, the increment is considered which any extensive property (I , 10), such as the volume, heat-capacity, heat-content, or free-energy content, of a solution of definite composition undergoes when one mol or one formular weight of one of its components is added to an infinite quantity of the solution, kept at constant temperature and pressure. This increment is called the *partial molar (or partial formular) volume, heat-capacity, heat-content, free energy*, etc., of the stated component in the specified solution at the specified temperature and pressure.

This definition of a partial molar quantity is evidently expressed analytically by the following equation in which G denotes the value of any extensive property of the solution (such as its volume, heat-capacity, heat-content, free energy), and in which $\tilde{G}_A, \tilde{G}_B, \dots$ denote the partial molar values of this property for the respective components A, B, $\dots$ in the specified solution:

$$\tilde{G}_A = \left(\frac{\partial G}{\partial N_A} \right)_{p, T, N_B, \dots}; \tilde{G}_B = \left(\frac{\partial G}{\partial N_B} \right)_{p, T, N_A, \dots}; \dots \quad (73)$$

The term *partial* is appropriately used for such quantities, because out of the partial molar values $\tilde{G}_A, \tilde{G}_B, \dots$ of a property for the separate components of a solution consisting of $N_A, N_B, \dots$ mols of components A, B, $\dots$ the value G of that property for the whole solution can be calculated by the equation:

$$G = N_A \tilde{G}_A + N_B \tilde{G}_B + \dots \quad (74)$$

This equation follows from the consideration that such a solution can actually be produced by adding successively N_A mols of A, N_B mols of B, etc., to an infinite quantity of the solution, and then cutting off from it such a quantity as contains N_A mols of A, N_B mols of B, etc. The equation expresses the *summation law of partial molar quantities*, which results directly from the definition of the concept.

In the thermodynamic treatment of solutions partial molar values of the heat-content and free energy of the components are especially useful. These are defined in the same way as for other properties; except that, since only differences in the magnitudes of these thermodynamic properties can be measured,

the values have to be referred to the value in some reference state. One method that is convenient in dealing with the physical relations between solutions and their components is to assume the heat-contents and free energies to be zero for the pure components in the most stable state at the same temperature and pressure. Then the *partial molar heat-contents* $\tilde{H}_A, \tilde{H}_B, \dots$ and *partial molar free energies* $\tilde{F}_A, \tilde{F}_B, \dots$ of the components A, B, $\dots$ in a solution at any temperature and pressure become equal to the heat-content increase or free-energy increase that attends the change in state (at that temperature and pressure) whereby one mol of the pure component and an infinite quantity of the solution are mixed to produce a correspondingly larger quantity of solution.

This heat-content increase can be derived from calorimetric measurements of the heat evolved upon mixing the pure component with finite quantities of solutions of various compositions. The free-energy increase has to be derived by considering some reversible process of mixing the pure component with an infinite quantity of the solution. Thus in case a component A has a measurable vapor-pressure, its partial molar free-energy $\tilde{F}_A$ in the solution can be shown, by considering the above formulated (IV, 39) reversible process of isothermal distillation of the pure component into an infinite quantity of the solution, to be expressed by the equations:

$$\tilde{F}_A = \int_{p_{A0}}^{p_A} \tilde{v} dp;$$

or

$$\tilde{F}_A = R T \ln \frac{p_A}{p_{A0}} \text{ (when solute vapor is perfect).} \quad (75)$$

**** Prob. 62. — Evaluation of Partial Molar Volumes from Density Data.** — From the density data at 20° and 1 atm. given below (*I.C.T.*, 3, 118) derive the partial molar volumes at 20° and 1 atm. of ethyl alcohol in aqueous solutions of the empirical compositions $C_2H_5OH.2H_2O$ and $C_2H_5OH.H_2O$ by calculating the data over into a suitable form, plotting the results on a large scale, and reading off the desired values.

Weight-percent alcohol	50	55	60	65	70	75
Density (in g./l.)	913.84	902.58	891.13	879.48	867.66	855.64

Tabulate the partial molar values obtained beside the molar volume (58.3) of pure ethyl alcohol at 20° and 1 atm.

**** Prob. 63. — Evaluation of Partial Molar Heat-Contents from Heats of Dilution.** — *a.* By reference to the heats of dilution given on page 70 (II, 12), plot values of the heat of solution of $1\text{ZnCl}_2(\text{s})$ in $N\text{H}_2\text{O}(\text{l})$ as ordinates and the corresponding values of N (ranging from $N = 20$ to $N = 400$) as abscissas. *b.* With the aid of this plot, determine the heat-effect attending the addition of $1\text{H}_2\text{O}(\text{l})$ to an infinite quantity of $1\text{ZnCl}_2 \cdot 100\text{H}_2\text{O}$. *c.* Derive a relation between the heat-effect attending the dissolving of $1\text{ZnCl}_2(\text{s})$ in $100\text{H}_2\text{O}(\text{l})$ (called its *integral* heat of solution), that attending the addition of $100\text{H}_2\text{O}(\text{l})$ to an infinite quantity of a solution of the composition $1\text{ZnCl}_2 \cdot 100\text{H}_2\text{O}$, and that attending the addition of $1\text{ZnCl}_2(\text{s})$ to an infinite quantity of such a solution (called its *partial* heat of solution). *d.* Evaluate the last named heat-effect. *e.* Estimate by extrapolation to infinite dilution the limiting value of the integral heat of solution of $1\text{ZnCl}_2(\text{s})$ in water, which must be equal to its partial heat of solution in $\text{ZnCl}_2 \infty \text{Aq}$. *f.* Calculate the partial formulär heat-content of ZnCl_2 in $1\text{ZnCl}_2 \cdot 100\text{H}_2\text{O}(\text{l})$,

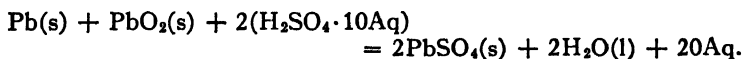
(1) taking that of $1\text{ZnCl}_2(\text{s})$ equal to its heat of formation, $-95,500$ cal.;

(2) taking that of $1\text{ZnCl}_2(\text{s})$ equal to zero; and

(3) taking that of 1ZnCl_2 in $\text{ZnCl}_2 \infty \text{Aq}$ equal to zero.

g. Calculate a value for the heat-content represented by the symbol $1\text{ZnCl}_2 \cdot 100\text{Aq}$ corresponding to each of the three reference states of ZnCl_2 defined in *f.* Note that use of the symbol Aq implies that the heat content of $1\text{H}_2\text{O}(\text{l})$ is taken equal to zero (II, 11).

**** Prob. 64. — Heat-Content Equations Involving Partial Molar Heat-Contents in Solution.** — The measured heat-evolution $-Q_p$ attending the mixing at 18° of $1\text{H}_2\text{SO}_4(\text{l})$ with $\text{NH}_2\text{O}(\text{l})$ is expressed by the empirical equation, $-Q_p = 18,800 N/(N + 1.80)$ for values of N not exceeding 20. Calculate the heat-evolution attending the addition to an infinite quantity of a solution of the composition $1\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, *a.* of $1\text{H}_2\text{O}(\text{l})$; *b.* of $1\text{H}_2\text{SO}_4(\text{l})$; *c.* From these two heat-effects and the heats of formation of $1\text{PbSO}_4(\text{s})$, $1\text{H}_2\text{SO}_4(\text{l})$, $1\text{PbO}_2(\text{s})$, and $1\text{H}_2\text{O}(\text{l})$, which at 18° are $-218,500$ cal., $-193,750$ cal., $-65,000$ cal., and $-68,370$ cal. respectively, calculate the increase in heat-content attending the change in state at 18° , $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{in } 1\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}) = 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{in } 1\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O})$. (This is the change in state which takes place in a lead storage cell corresponding to the passage through it of 2 faradays of electricity.) *d.* Calculate for comparison the increase in heat-content attending the change in state,



**** 41. Relation between the Partial Molar Quantities of a Two-Component System.** — Another useful principle in regard to partial molar quantities can be derived from their definition (Eq. 73) and from the summation law (Eq. 74) expressing the total value G of any extensive property of a two-component system. This principle is expressed by the following equation:

$$X_A d\tilde{G}_A + X_B d\tilde{G}_B = 0;$$

or

$$d\tilde{G}_B = - \frac{X_A}{1 - X_A} d\tilde{G}_A; T, p, \text{ constant.} \quad (76)$$

In this equation $d\tilde{G}_A$ and $d\tilde{G}_B$ denote the increments of the partial molar values for the two components in a specified solution at any definite temperature and pressure produced by changes dX_A and dX_B in the mol-fraction of the components. This principle is expressed in partial derivatives as follows:

$$X_A \left(\frac{\partial \tilde{G}_A}{\partial X_A} \right)_{p, T} + X_B \left(\frac{\partial \tilde{G}_B}{\partial X_A} \right)_{p, T} = 0;$$

or

$$\left(\frac{\partial \tilde{G}_B}{\partial X_A} \right)_{p, T} = - \frac{X_A}{1 - X_A} \left(\frac{\partial \tilde{G}_A}{\partial X_A} \right)_{p, T}. \quad (77)$$

The relation just formulated can be derived in the following way (*Lewis, Randall, 1923*). Differentiating the equation expressing the summation law (Eq. 74), which is an entirely general expression for the value of any extensive property of a two-component solution as a function of four variables ($\tilde{G}_A$, $\tilde{G}_B$, N_A , N_B), there results:

$$dG = \tilde{G}_A dN_A + N_A d\tilde{G}_A + \tilde{G}_B dN_B + N_B d\tilde{G}_B. \quad (78)$$

Considering now that the change dG in the property is produced at constant temperature and pressure, that is, by a change only in the number of mols of the respective components in the solution, we have, in virtue of the definition of partial molar quantities;

$$dG = \tilde{G}_A dN_A + \tilde{G}_B dN_B. \quad (79)$$

Combination of these two equations yields:

$$N_A d\tilde{G}_A + N_B d\tilde{G}_B = 0;$$

or

$$N_A d\tilde{G}_A = - N_B d\tilde{G}_B; T, p, \text{ constant.} \quad (80)$$

Finally, introducing the mol-fraction X_A , which is equal to $N_A/(N_A + N_B)$, there results the previously formulated relation (Eq. 76) between the partial molar values of the two components.

**** 42. Relation between the Partial Molar Free Energies and Duhem's Equation.** — An important chemical application of the relation between partial molar values is that afforded by the following expression (*Gibbs, 1876*) for the changes in the partial molar free energies $\tilde{F}_A$ and $\tilde{F}_B$ of a two-component system with the mol-fraction X_A at constant temperature and pressure:

$$\frac{d\tilde{F}_B}{dX_A} = - \frac{X_A}{1 - X_A} \frac{d\tilde{F}_A}{dX_A}. \quad (81)$$

This equation evidently enables the partial molar free energy of one component to be calculated from that of the other component when the change of the latter with the composition of the solution is known. This is useful in applications of chemical thermodynamics.

From this partial molar free-energy relation (Eq. 81), moreover, there can be derived *Duhem's equation*, already incidentally referred to (Eq. 54; IV, 29). This is done merely by substituting in Eq. 81 for $d\tilde{F}_A$ and $d\tilde{F}_B$ the quantities $RT d \ln p_A$ and $RT d \ln p_B$ (Eq. 75; IV, 40). The equation (*Duhem, 1886*) can be written, not only in the symmetrical form given above, but in various other forms. Of these the following, applicable where the vapors are perfect gases, is convenient for practical use:

$$\frac{d \ln p_B}{dX_A} = - \frac{X_A}{1 - X_A} \frac{d \ln p_A}{dX_A} (T, p, \text{ constant}). \quad (82)$$

By application of this equation to solutions with two volatile components the change of the vapor-pressure of one component with the mol-fraction can be derived from the change in the vapor-pressure of the other component.

The accuracy of Duhem's equation is not dependent on the concentration of the solution; but it is inexact insofar as error arises from deviations of the pressure of the vapors from

the perfect-gas laws. Duhem's equation is also slightly inexact unless the solution is kept under a constant pressure (p_L) when its mol-fractions are varied; yet the effect of pressure on vapor-pressure is so small that the equation is substantially accurate when the solution is always under pressures equal to its total vapor-pressures.

**** Prob. 65.** — *Vapor-Pressure of One Component of a Solution Derived from That of the Other Component by Duhem's Equation.* — *a.* Derive from Eq. 82 the following relation between the Raoult-law deviations of one of the components B at the mol-fractions X_{B_g} and X_{B_l} and those of the other component A at the intermediate mol-fractions X_A :

$$\ln \frac{p_{B_g}/p_{B_0} X_{B_g}}{p_{B_l}/p_{B_0} X_{B_l}} = - \int_1^2 \frac{X_A}{1 - X_A} d \ln (p_A/p_{A_0} X_A).$$

b. Assuming that the Raoult-law deviations of component A are known for a series of mol-fractions between X_{A_l} and X_{A_g} , and that the deviation of component B is known at one of these limiting mol-fractions X_{B_l} describe a graphic method by which the deviation of its value at the other limiting mol-fraction X_{B_g} can be determined. *c.* Derive the vapor-pressure of acetone at 35.17° in a mixture of 26.80 mol-percent of chloroform and 73.20 mol-percent of acetone from the vapor-pressure (344.5 mm.) of acetone in the pure state and from the following vapor-pressures of chloroform in its mixtures with acetone (*Zawidzki, 1900*):

Mol-percent chloroform	5.95	12.17	18.35	26.80	100
Vapor-pressure	9.3	20.1	31.8	50.4	293.1 mm.

Tabulate this result beside the observed vapor-pressure (240.6 mm.) of acetone in the mixture containing 26.8 mol-percent of chloroform. *Ans.* 242.5 mm.

43. The Concept of Activity and Its Relation to Molar Free Energy. — The activity of any chemical or molecular species (I, δ) is an intensive property which is of great importance in the thermodynamic treatment of chemical equilibrium. Its relation to molar free energy will now be considered.

The *activity* a_A of any molecular species A in a solution or phase of definite chemical composition, pressure, and temperature may be defined in terms of its molar free energy $\tilde{F}_A$ by the equation,

$$\tilde{F}_A = R T \ln a_A + K. \quad (83)$$

In this equation K is a constant with respect to changes in composition of the solution and to changes in the pressure applied to it, but varies with the temperature. This definition does not suffice for determining the absolute value of the activity of a molecular species, since the free energy itself and the constant K are indeterminate. It follows from it, however, that the molar free energy of transfer at constant temperature of the molecular species A between two solutions or phases of different composition, in which its activities are a_1 and a_2 , respectively, is given by the equation,

$$-\Delta\tilde{F}_A = \tilde{F}_{A_1} - \tilde{F}_{A_2} = R T \ln (a_1/a_2). \quad (84)$$

The equation shows that the molar free energy of transfer, which can be evaluated from various types of equilibrium studies, affords a quantitative measure of the relative activities in different solutions or phases at the same temperature. Thus, if the activity of A is a_0 in some solution or phase, selected as a standard reference state (IV, 40) of the substance * in which the molar free energy of A is $\tilde{F}_A^0$, its activity a in any other solution or phase at the same temperature in which its molar free energy is $\tilde{F}_A$ is expressed by the equation,

$$\tilde{F}_A - \tilde{F}_A^0 = R T \ln (a/a_0). \quad (85)$$

The numerical value for the *relative activity* (a/a_0) thus defined evidently depends on the choice of the reference state of the substance. It represents the activity of A referred to its activity arbitrarily taken as unity in some conveniently chosen *standard state* of the substance. Each substance is considered to have at each temperature a series of standard states, which will be discussed in the next article.

It is evident that the numerical value assigned to the molar free energy $\tilde{F}_A^0$ of A in a specified standard state will depend on the zero-point adopted for the free-energy scale. In correspondence with the convention as to the arbitrary zero-point of the heat-content scale (II, 11), the molar free energy $\tilde{F}_A^0$ of the substance at any definite temperature in any one of its several standard states of unit activity is usually considered equal

* By substance is here meant that component (I, 16) of the solution or phase which supplies the molecular species A under consideration (I, 8).

to the free energy increase per mol that attends its formation out of the pure elementary substances at the same temperature, and at a pressure of one atmosphere, each elementary substance being in the state of aggregation that is the stable one at this temperature and pressure. It will be shown later (IV, 46) that the molar free energies of different substances in their various standard states are closely related to the free energy and the equilibrium conditions of chemical reactions. It may be pointed out here that changes in free energy at any definite temperature are conveniently represented by free energy equations similar in every respect to heat-content equations.

44. Standard States of Reference for Activity. — In the thermodynamic treatment of chemical equilibrium it is of great importance to be able to determine how at some definite temperature the activity of a particular molecular species A in a gaseous, liquid, or solid solution varies with the composition of the solution, and with the applied pressure. As a basis of reference for evaluating the activity of A in any such solution of definite composition and pressure, each substance is considered to have at each temperature a series of standard states; namely, it has one reference state when it is a component of a gaseous solution, and certain others when it is present as solute (or solvent) in a liquid or solid solution. Such standard states are specifically described below. It will there be shown that these are so chosen that the laws of perfect solutions and perfect gases relating to the equilibrium distribution of a specified molecular species between the phases of an isothermal system can be applied without error to concentrated solutions and to gases at high pressures by the simple expedient of substituting activities as above defined for the pressures, concentrations or mol-fractions which occur in the expressions for the distribution constants. From this point of view the activity of a solute (or solvent) represents, and is often defined as its effective concentration (or mol-fraction) in determining the equilibrium with the vapor in accordance with Henry's law (or Raoult's law); and correspondingly the activity of the molecular species in the vapor phase may be defined as its effective pressure in determining its equilibrium concentration (or mol-fraction) in the liquid (or solid) solution.

In this text the activity of any particular species in a liquid (or solid) solution will be shown by enclosing within a bracket its molecular formula, and, when present in a gaseous solution, by the letter f with a subscript to describe the species.* Thus, the activity of Cl_2 in an aqueous solution will be designated $[\text{Cl}_2]$ to distinguish it from its molal concentration shown as (Cl_2) ; whereas, if present in a gas phase, its (relative) activity (or fugacity) will be designated f_{Cl_2} to distinguish it from its partial pressure p_{Cl_2} , expressed in atmospheres.

Standard States of a Substance at a Specified Temperature.

(1) *As Solvent.* — The standard state of unit-activity of the solvent in a liquid (or solid) solution is the pure liquid (or solid) substance under an applied pressure of one atmosphere. The specification that the applied pressure is one atmosphere is relatively unimportant in this case, since the effect of pressure on the molar free energy (II, 23), and hence on the activity of the liquid (or solid) solvent is usually negligibly small in comparison with the effect of the added solute.

It can be readily shown, as in Prob. 66, that the activity of the solvent in any solution is on this basis equal to the ratio p_A/p_{A0} of its vapor-pressure in the solution to that of the pure solvent.† For all Raoult-law solutions the activity of the solvent is evidently equal to the solvent mol-fraction in the solution, and for all dilute solutions it is nearly equal to unity. For any concentrated non-ideal solution the ratio $[A]/X_A$ of the activity of the solvent to its mol-fraction differs from unity by an amount equal to the fractional extent to which the solvent vapor-pressure deviates from Raoult's law. This ratio, appropriately designated the deviation-coefficient (IV, 35), is more commonly called the *activity-coefficient* of the solvent. It is the factor α by which the solvent mol-fraction must be multiplied in order to obtain the activity (or effective mol-fraction) of the solvent in the solution. It follows from the above considerations that Raoult's law in corrected form may be expressed by the equation,

$$p_A = p_{A0} X_A \alpha_A = p_{A0} [A] \quad (\text{when the solvent vapor is perfect}). \quad (86)$$

Prob. 66. — Activity of the Solvent in Relation to Its Vapor-Pressure. — *a.* By a reversible process of isothermal distillation

* The relative activity of a molecular species in a gas phase is equal to its so-called fugacity, f .

† A small correction must be applied (Eq. 15; IV, 8) when the vapor is imperfect.

(IV, 8; Prob. 13a) derive an expression for the free energy decrease attending the addition of 1 mol of solvent of vapor-pressure p_{A0} to an infinite quantity of a solution in which the solvent vapor-pressure is p_A . *b.* Through comparison of the result with Eq. 85, show that the activity of the solvent in the solution referred to its standard state of unit activity is equal to the ratio p_A/p_{A0} . *c.* State any simplifying assumption made in the derivation, and suggest a procedure for obtaining a more exact relation.

Prob. 67. — Activity of Solvent from Freezing-Point Lowering. — Calculate the activity of H_2O in a solution 1.0 wf. in NaCl at 0° , which shows a freezing-point lowering 1.79 times that caused by an unionized perfect solute at that concentration. *Ans.* 0.97.

(2) *As Solute.* — The choice of a standard state to which the activity of a solute in a specified solvent may be referred is based on the following considerations.

It has been shown (IV, 39; Eq. 70) that the molar free energy of transfer of a volatile solute A between two solutions of different composition, in which the solute vapor-pressures are p_{A1} and p_{A2} , is equal to $RT \ln (p_{A1}/p_{A2})$ when the solute vapor is perfect. It follows from this and Eq. 84 that the activity a_A , and hence also the relative activity $[A]$ of the volatile solute is proportional to its vapor-pressure as expressed by the equation,

$$[A] = \text{Const. } p_A \text{ (when the solute vapor is perfect).} \quad (87a)$$

The equation is exact for solutions which at high concentrations show large deviations from Henry's law; and even when the concentration of the molecular species is unknown, it permits relative values of activity to be derived from vapor-pressure measurements. Thus the ratio of the activities of NH_3 at 20° in solutions of the empirical composition $1 NH_3 \cdot 8.5 H_2O$ and $1 NH_3 \cdot 21 H_2O$ is known to be 2.96, since the vapor-pressures of NH_3 in those solutions are 80 and 27 mm. respectively; yet the concentration of NH_3 as such is entirely unknown because of lack of knowledge as to the extent to which it is converted by hydration into NH_4OH . Similarly, the activity of HCl at 25° in 10 formal aqueous solution is 30 times its activity in a 6 formal solution since the vapor-pressures of HCl in these two solutions are 4.20 and 0.14 mm., respectively; even though nothing is known about the concentration of HCl as such because of uncertainty as to the extent of hydration and ionization in the solutions. The value of the proportionality constant in Eq. 87a is, however, dependent on the choice of the standard state of the volatile solute to which its activity is referred. For practical reasons the choice is usually limited to one or other of the two standard states described below.

a. The standard state is so chosen that, as the weight-molality (A) approaches zero in a solution under an applied pressure of one

atmosphere, the ratio $[A]/(A)$ of its activity to its weight-molality approaches unity. The specification of an applied pressure of one atmosphere is relatively unimportant, since the effect of pressure on the molar free energy of the solute is usually negligible in evaluating its activity.

On this basis the activity $[A]$ of the solute at infinite dilution becomes identical with its weight-molality (A) , and Eq. 87a may be written in the form;

$$[A] = (A)\alpha_A = K p_A \text{ (when the solute vapor is perfect).} \quad (87b)$$

The proportionality constant K is thereby made identical with the distribution constant in Henry's law as expressed by Eq. 53 (IV, 27). The ratio $[A]/(A)$, called the activity-coefficient α_A of the solute, differs from unity by the fractional extent to which the solute vapor-pressure deviates from Henry's law. It is the factor by which the solute concentration must be multiplied in order to obtain its activity (or effective concentration) in the solution.

The standard state of unit-activity of the solute is in this case a hypothetical one. It may be considered to represent its state as a perfect solute when dissolved in the specified solvent at a concentration one weight-molal. That is to say, not only is its activity unity, but its partial molar volume, heat-content, and heat-capacity are the same as in the infinitely dilute solution.

It is evident that the standard state of the solute might equally well be considered to represent its state as a perfect solute at a concentration one volume-molal, instead of one weight-molal. It is often convenient to do so.

b. The standard state is so chosen that, as the solute mol-fraction approaches zero, the ratio $[A]/X_A$ of its activity to its mol-fraction approaches unity. The applied pressure is, as before, specified to be one atmosphere.

On this basis the activity $[A]$ of the solute at infinite dilution becomes identical with the mol-fraction X_A , and Eq. 87a may be written in the form:

$$p_A = K_X[A] = K_X X_A \alpha_A \text{ (when the solute vapor is perfect).} \quad (87c)$$

The proportionality factor K_X in this equation is thus made identical with the distribution constant in Henry's law as expressed by Eq. 52 (IV, 27). The ratio $[A]/X_A$, or activity-coefficient α_A of the solute, differs from unity by the fractional extent to which the solute vapor-pressure differs from Henry's law.

Here again, in the hypothetical state of unit-activity the partial molar volume, heat-content, and heat-capacity are the same as in the infinitely dilute solution. It may be noted that in the case of an ideal solution, the distribution constant K_X is equal to

the vapor-pressure of the solute A in the state of a pure liquid, and its standard state becomes identical with that described for A when it was considered to be the solvent.

Prob. 68. — Activity of Solute in Relation to Its Vapor-Pressure. — a. Calculate the ratio of the activities of NH_3 in 1.0 vf. and 0.1 vf. solution at 25° from its vapor-pressures in these solutions which are 13.45 and 1.327 mm. *b.* In the 0.1 vf. NH_3 solution 1.3% of the dissolved NH_3 reacts with H_2O to form $\text{NH}_4^+ + \text{OH}^-$, and an unknown proportion to form NH_4OH . In correspondence with the modified form of Henry's law as applied to a partially solvated solute (IV, 27), the standard state of dissolved NH_3 is so chosen that its activity $[\text{NH}_3]$ in dilute solution (here considered to be 0.1 vf. or less) is equal to $(\text{NH}_3) + (\text{NH}_4\text{OH})$, the sum of the molal concentrations of NH_3 and NH_4OH . The activity-coefficient of NH_3 is thereby defined by the ratio $[\text{NH}_3]/((\text{NH}_3) + (\text{NH}_4\text{OH}))$. Calculate the activity of NH_3 in 1.0 vf. NH_3 at 25° , and its corresponding activity-coefficient under the assumption that the proportion converted to ionized NH_4OH is negligible. *c.* Addition of 1 KCl to one liter of the 1.0 vf. NH_3 solution increases the vapor-pressure of NH_3 to 15.53 mm. Calculate the corresponding activity and activity-coefficient of the dissolved ammonia. *d.* At 25° a carbon tetrachloride solution 0.004 vf. in NH_3 is in equilibrium with an aqueous solution 1.0 vf. in NH_3 . Calculate the concentration of NH_3 in a carbon tetrachloride solution which is in equilibrium at 25° with an aqueous solution 1.0 vf. in KCl and 1.0 vf. in NH_3 .

(3) *As Constituent of a Gaseous Solution. —* The activity of a molecular species A in a gaseous solution is referred to the activity of that species in the state of a perfect gas, in which state its activity is made equal to its pressure p_A . The corresponding standard state of unit-activity is in this case a hypothetical one in which the gas is at a pressure of one atmosphere and still retains the properties of a perfect gas. Thus, in this imagined state the molar volume of A is that calculated by the perfect-gas equation (I, 14), and its molar heat-content and heat-capacity are by the laws of perfect gases (II, 9) equal to the limiting values which these properties approach as the pressure of the gas approaches zero. The activity of A when so defined is called its *fugacity* (G. N. Lewis, 1901).* On this basis the ratio f_A/p_A of the fugacity

* The activity of A in a liquid (or solid) solution may also be referred to its standard state of unit-activity in a gaseous solution. The corresponding activity of A is then called its fugacity in the liquid (or solid) solution. As the name implies the fugacity of A (like its molar free energy) affords a practical measure of its tendency at a specified temperature to escape from one phase of a heterogeneous system to another. At equilibrium its fugacity (like its vapor-pressure (II, 25)) in any one phase must be equal to that in any other phase of an isothermal system.

of A in a gas phase to its partial pressure approaches unity as the total pressure approaches zero. This ratio is called the activity-coefficient α_A of A.

When the gas A is not mixed with other gaseous substances its fugacity at any pressure may be derived from its equation of state. Thus, when the gas is expanded isothermally from a specified pressure p_A , where its fugacity is f_A , to some lower pressure p'_A , where its fugacity is f'_A , the molar free energy decrease is,

$$-\Delta \tilde{F}_A = \int_{p'_A}^{p_A} \tilde{v} dp = R T \ln \frac{f_A}{f'_A}.$$

It follows from this relation and the equation of state (III, 4), $p \tilde{v} (1 - \beta p) = R T$, that,

$$\int_{p'_A}^{p_A} \tilde{v} dp = R T \ln \frac{p_A / (1 - \beta p_A)}{p'_A / (1 - \beta p'_A)}$$

and, therefore, that

$$\frac{p_A / (1 - \beta p_A)}{p'_A / (1 - \beta p'_A)} = \frac{f_A}{f'_A}.$$

But, as p'_A approaches zero, both $(1 - \beta p'_A)$ and the ratio f'_A/p'_A approach unity. Consequently, the fugacity of A at the specified pressure is given by the equation,

$$f_A = \frac{p_A}{1 - \beta p_A} = \alpha_A p_A. \quad (88)$$

This equation may be used without large error to calculate the fugacity of A, and its corresponding activity-coefficient, even up to high pressures. The deviation-coefficient β may be computed at each temperature (Eq. 49; III, 27) from the constants a and b occurring in van der Waal's equation.

In deriving an exact expression for the fugacity of a gas at high pressures, it is convenient to express the deviation D of the $p v$ -product from $R T$ as a power function of the pressure, as shown by an equation of state of the form,

$$p \tilde{v} = R T + D = R T + M p + N p^2 + O p^3 + \dots \quad (89)$$

The constants, M , N , and O , in this equation vary with the temperature, and may be computed at each temperature (*Beattie, Bridgeman, 1928*) from the van der Waal constants, a and b , and three other empirical constants characteristic of the gas. It follows from Eq. 89 (as shown in Prob. 70) that the fugacity f_A of gaseous A, and its corresponding activity-coefficient α_A , at pres-

sure p_A may be calculated from the equation,

$$\ln \frac{f_A}{p_A} = \ln \alpha_A = \frac{1}{RT} \int_0^{p_A} \frac{D}{p} dp. \quad (90)$$

Prob. 69. — The Fugacity of an Imperfect Gas at Moderate Pressures. — At 0° and 1 atm. the molar volume of ammonia is less than the perfect gas value by 1.51%. *a.* Calculate the activity-coefficient of ammonia at 0° and 2 atm. *b.* Calculate the difference, $\tilde{F}_{\text{NH}_3} - \tilde{F}_{\text{NH}_3}^0$, between the molar free energy of ammonia at 1 atm. and that in its standard state as a gas at 0° .

Prob. 70. — The Fugacity of a Gas at High Pressures. — *a.* Derive Eq. 90 from Eq. 89. Note that by definition of the standard state the activity-coefficient of a gas approaches unity as its pressure approaches zero. *b.* Calculate the activity-coefficient of CO_2 at 60° at the respective pressures 10, 20, 40, and 80 atm. by each of the following methods, and tabulate the results:

(1) From the tabulated experimental data (*Amagat, 1893*) relating to CO_2 at 60° , by graphical integration of $(D/p) dp$ from zero to p . Note that as p approaches zero, the volume-difference, $\tilde{v} - RT/p$, approaches a finite limiting value.

Pressure, p	13.01	35.42	53.65	74.68	85.35 atm.
Molar-volume, $\tilde{v}$	2000.0	666.7	400.0	250.0	200.0 ml.
$RT/p = 27,337/p$	2101.2	772.0	509.4	366.1	320.4

(2) From the equation of state (*Beattie, Bridgeman, 1928*) for CO_2 at 60° , $p\tilde{v} = RT - 96.23p - 0.2066p^2 + 0.00117p^3$.

(3) From the equation of state $p\tilde{v}(1-\beta p) = RT$, computing the deviation-coefficient β from the van der Waal constants for CO_2 , $b = 98.6$ and $a = 5.96 \times 10^6$ (Table VIII; III, 27).

A precise value for the fugacity of gas A mixed with other gases can not be calculated without a comprehensive knowledge of the pressure-volume relations at the specified temperature of mixtures containing the components in varying proportions. An approximate value can, however, be computed under the reasonable assumption (*G. N. Lewis, 1908*) that the fugacity of A in the mixture at a specified temperature and pressure p is proportional to its own mol-fraction X_A , as expressed by the equation,

$$f_A = f_{A_0} X_A = \alpha_{A_0} p X_A.$$

In this equation f_{A_0} is the fugacity of A when present alone at the specified pressure p , and α_{A_0} is the corresponding activity-coefficient. The product $p X_A$ is the partial pressure of A in the mixture as calculated by Dalton's law (III, 7).

X. THE MASS-ACTION LAW OF CHEMICAL EQUILIBRIUM AND ITS THERMODYNAMIC DERIVATION.

45. The Mass-Action Law of Chemical Equilibrium. —

The effect of concentration in determining chemical equilibrium is expressed by one of the most fundamental laws of chemistry. This law, which is commonly known as the *mass-action law*, is presented in this chapter because, as shown by its derivation in the next article, at any definite temperature the equilibrium conditions of a chemical reaction are closely related to the partial molar free energies (or *chemical potentials* per mol) of the reactants and reaction-products in the equilibrium mixture. Applications of the law to various types of chemical equilibria will be fully considered in Chapter VII.

The mass-action law states that, whatever be the initial concentrations of the gaseous or dissolved substances A, B, ... E, F, ... involved in any definite chemical reaction, such as may be represented in general by the equation, $aA + bB \cdots = eE + fF \cdots$, the reaction always takes place in such a direction and to such an extent that, when equilibrium is reached at any definite temperature, the conditions are satisfied which are expressed by the equation:

$$\frac{(E)^e (F)^f \cdots}{(A)^a (B)^b \cdots} = K_e, \text{ (a constant).} \quad (91a)$$

In this expression (E), (F), ... (A), (B), ... denote the molal concentrations of the molecular species E, F, ... A, B, ... in the equilibrium mixture, and $e, f, \cdots a, b, \cdots$ denote the number of mols of them that are involved in the reaction expressed by the chemical equation.

The quantity K_e , which is a constant characteristic of the reaction, is called its *equilibrium-constant*. Its value is, of course, constant with respect to variations of the initial or equilibrium concentrations, but it varies with the temperature. In evaluating it, volume-molalities will be used in the case of gaseous solutions, and weight-molalities (IV, 1) in the case of liquid solutions. It is customary to place in the numerator the concentrations of the substances occurring on the right-hand side of

the chemical equation written in some specified way. In which direction the chemical equation is written is, of course, arbitrary in the case of reactions at equilibrium. With many types of reactions, however, it is more natural to write the equation in one of the two directions; and in such cases the usage in evaluating the equilibrium-constant has become fairly definite. This usage will be illustrated by the examples given later.

The mass-action law when applied to dilute liquid solutions is sometimes expressed in the alternative form,

$$\frac{X_B^c X_F^f \cdots}{X_A^a X_B^b \cdots} = K_X, \text{ (a constant).} \quad (91b)$$

The substitution of the mol-fractions $X_B, X_F, \cdots X_A, X_B, \cdots$ for the corresponding weight-molalities in evaluating the equilibrium constant K_X is admissible, since, as the mol-fraction $N/(N_o+N)$ approaches zero, it becomes equal to the mol-ratio N/N_o , and this is proportional to the weight-molality of the solution.

In applications of the mass-action law to gases, it is usual to substitute for the concentrations of the substances in the equilibrium-mixture their partial pressures. This is admissible since at any definite temperature the two quantities are proportional to one another in the case of perfect gases, in virtue of the relation $p = c_v R T$.

The general mass-action expression in terms of partial pressures evidently is,

$$\frac{p_B^c p_F^f \cdots}{p_A^a p_B^b \cdots} = K_p, \quad (92)$$

where K_p is a constant, called the equilibrium-constant in terms of pressure, which has in general a different numerical value from the constant K_c occurring in the corresponding concentration-expression. In evaluating it the partial pressures are commonly expressed in atmospheres.

Prob. 71. — Relation Between the Equilibrium Expressions in Terms of Concentrations and Pressures. — Derive the general mass-action expression in terms of pressure from that in terms of concentration, and show the relation between the two equilibrium-constants K_p and K_c for gas reactions.

From a kinetic point of view the equilibrium conditions of a chemical reaction are satisfied when the concentrations (A), (B) ... (E), (F) ... are such that the rate of the direct reaction (involving the interaction of a molecules of A and b molecules of B, ...) is equal to that of the reverse reaction (involving the interaction of e molecules of E and f molecules of F, ...). In accordance with this view, it will be shown later (VI, 5) that the mass-action law of equilibrium is a consequence of a mass-action law of reaction-rate. It can also be derived with the aid of the laws of thermodynamics from the physical laws of perfect gases and of perfect solutions as shown in the next article. It has also been established by experimental investigations on the equilibrium conditions of a large number of different reactions.

The mass-action law, as expressed by Eqs. 91 (a, b), 92, is exact only in the case of reactions between perfect gases and perfect solutes. It holds true with reasonable accuracy in the case of most gases up to moderate pressures (such as 1 or 2 atmospheres), and in the case of solutes with electrically neutral molecules up to moderate concentrations (such as 1 molal), but shows large deviations in the case of electrically charged molecules or ions (V, 1-7) even at small concentrations (such as 0.01 molal for univalent ions, or 0.002 molal for bivalent ions). The law can be made exact, as shown in the next article, by substituting activities and fugacities, as defined in IV, 44, for the corresponding molal concentrations or partial pressures of the molecular-species in the expressions for the equilibrium constants. Thus, the equilibrium conditions of the reaction just considered are exactly expressed by the equations:

$$K_a = \frac{[E]^e [F]^f}{[A]^a [B]^b} = \frac{(E)^e (F)^f}{(A)^a (B)^b} \cdot \frac{\alpha_E^e \alpha_F^f}{\alpha_A^a \alpha_B^b} \quad (93a)$$

$$K = \frac{[E]^e [F]^f}{[A]^a [B]^b} = \frac{X_E^e X_F^f}{X_A^a X_B^b} \cdot \frac{\alpha_E^e \alpha_F^f}{\alpha_A^a \alpha_B^b} \quad (93b)$$

$$K_f = \frac{f_E^e f_F^f}{f_A^a f_B^b} = \frac{p_E^e p_F^f}{p_A^a p_B^b} \cdot \frac{\alpha_E^e \alpha_F^f}{\alpha_A^a \alpha_B^b} \quad (94)$$

Various experimental methods for determining the activity-coefficients (IV, 44) occurring in these equations will be described

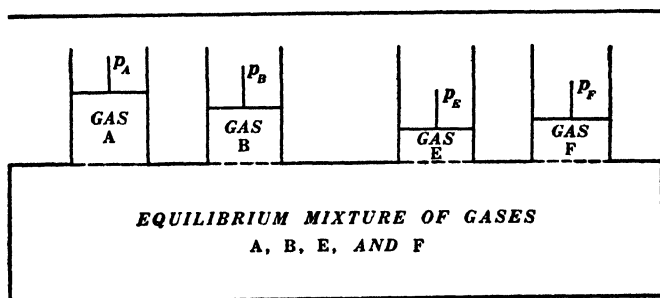
in later chapters. In subsequent applications of the mass-action law, however, it will, unless otherwise specified, be assumed that the substances involved in the chemical equilibrium behave as perfect solutes or gases, in which case the activity coefficients are by definition unity.

46. Thermodynamic Criteria of Chemical Equilibrium.

Derivation of the Mass-Action Law. — It has already been stated (II, 23) that the free energy decrease must be equal to zero for any isothermal change taking place under conditions which are substantially those at which equilibrium prevails within the system; but heretofore this has been proved for physical changes only (such as fusion, crystalline transition or vaporization). It will now be shown that this general criterion of equilibrium conditions applies also to chemical changes.

Consider any chemical reaction $aA + bB \cdots = eE + fF \cdots$ between the gaseous substances A, B, $\cdots$ E, F $\cdots$ to take place reversibly at any definite temperature T with the aid of the apparatus shown in Figure 8. This consists of a reservoir

FIGURE 8. A CHEMICAL REVERSIBLE PROCESS.



and a number of cylinders which communicate with it through walls, each of which is permeable to only one of the gases. The cylinders, which serve to hold the separate gases, are provided with weighted frictionless pistons. The reservoir contains a mixture of the gases at any partial pressures $p_A, p_B \cdots p_E, p_F \cdots$ at which the chemical change is in equilibrium. Each piston is so weighted that the pure gas in the cylinder is in equilibrium with that same gas in the mixture in the reservoir. This whole

apparatus is placed in a heat reservoir of practically infinite heat-capacity at a uniform temperature T ; and this reservoir, and the weights on the pistons constitute the surroundings where the work and heat effects occur.

Starting now with a mols of A, b mols of B $\cdots$ in their respective cylinders at the equilibrium pressures $p_A, p_B \cdots$, consider the following process to be carried out at the temperature T under reversible conditions, always keeping the external pressure on any piston within an infinitesimal amount of the gas beneath it. Force a mols of A, b mols of B $\cdots$ into the reservoir, at the same time drawing out into the other cylinders at the equilibrium pressures $p_E, p_F, \cdots$ the e mols of E and f mols of F $\cdots$ which must form spontaneously out of A, B, $\cdots$ in order that equilibrium in the mixture may be maintained. The resultant change in state is briefly expressed by the equation:

$$aA \text{ (at } p_A) + bB \text{ (at } p_B) \cdots = eE \text{ (at } p_E) + fF \text{ (at } p_F) \cdots$$

For this change in state,

$$-\Delta A = W_R = (e p_E \tilde{v}_E + f p_F \tilde{v}_F) - (a p_A \tilde{v}_A + b p_B \tilde{v}_B) = \Delta \Sigma (p v),$$

and therefore, by Eq. 40 (II, 22),

$$-\Delta F = (a \tilde{F}_A \text{ (at } p_A) + b \tilde{F}_B \text{ (at } p_B)) - (e \tilde{F}_E \text{ (at } p_E) + f \tilde{F}_F \text{ (at } p_F)) = 0.$$

This relation is independent of the composition or pressure of the particular equilibrium mixture selected, and of the equation of state of the separate gases. It may also be noted that the molar free energy of each pure gas in the cylinder must be equal to its partial molar free energy in the equilibrium mixture. Accordingly, in any gaseous mixture of A, B, $\cdots$ E, F, $\cdots$ at any definite temperature T , the reaction will take place in one direction or the other, thereby changing the molal proportions of reactants and reaction-products until at equilibrium at any pressure p , the partial molar free energies $\tilde{F}_A, \tilde{F}_B \cdots \tilde{F}_E, \tilde{F}_F \cdots$ have values which satisfy the equation:

$$F_1 = a \tilde{F}_A + b \tilde{F}_B \cdots = e \tilde{F}_E + f \tilde{F}_F \cdots = F_2. \quad (95)$$

In other words, the reaction tends to take place with a decrease in the free energy of the system until at equilibrium the free

energies of the reaction-products became equal to, and just balance the free energies of chemically equivalent quantities of the reactants. It is often the case, however, that in spite of a strong thermodynamic tendency for change, the reaction may take place very slowly, and in extreme cases practically not at all. For example, a mixture of 2 mols of H_2 and 1 mol of O_2 at 25° and 1 atm. has considerably more free energy than does this same system in the state of 1 $\text{H}_2\text{O}(\text{l})$ at 25° and 1 atm.; yet chemical union does not take place (I, 17) at 25° and 1 atm. without the presence of some catalyst.

This law of chemical equilibrium also applies when the substances involved in the reaction are in the dissolved state in any specified solvent. For proof of this statement consider that at any definite temperature A, B, $\dots$ E, F, $\dots$ dissolved in water react to satisfy the equilibrium conditions of the reaction, and that the resultant aqueous solution is in equilibrium with a gaseous mixture at the same temperature containing the same substances in equilibrium proportions. Now by the laws of physical equilibrium the partial molar free energy of each substance in the aqueous solution is equal to its partial molar free energy in the gaseous solution, and hence Eq. 95, which has been shown to be a criterion of the chemical equilibrium in the gaseous solution, must also apply to the conditions of chemical equilibrium in the liquid solution. Although this proof involves the assumption that A, B, $\dots$ E, F, $\dots$ have appreciable vapor-pressures in the liquid solution, the conclusion drawn can hardly depend on the volatility of the substances. In fact it can be readily shown that Eq. 95 (*Gibbs, 1875-76*)* is an important criterion of the equilibrium conditions of any homogeneous, or heterogeneous reaction, however complicated. It applies, for example, to the equilibrium of the reaction $\text{AgCl}(\text{s}) + 2 \text{NH}_3(\text{g}) = \text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^-$ in aqueous solution. Thus when NH_3 in a gas phase by solution and chemical reaction reaches at any definite temperature T a state of equilibrium with solid AgCl and with the complex-salt $\text{Ag}(\text{NH}_3)_2\text{Cl}$, or with its ions, in an aqueous solution which is kept saturated with silver chloride, this fundamental law of chemical equilibrium requires that $\tilde{F}_{\text{AgCl}}(\text{s}) + 2 \tilde{F}_{\text{NH}_3}$

* In the Gibbs system partial molar free energies are called *chemical potentials*.

(in gas phase) = $\tilde{F}_{\text{Ag}(\text{NH}_3)_2\text{Cl}}$ (in aqueous solution) = $\tilde{F}_{\text{Ag}(\text{NH}_3)_2}^+ + \tilde{F}_{\text{Cl}^-}$ (in aqueous solution).

From the broad generalization that the same system in different equilibrium states at the same temperature must have the same free energy, may be derived, as indicated below, an important relation between the free energy decrease attending any chemical change in state at constant temperature and the equilibrium conditions of the reaction involved. From this relation may then be derived the mass-action law of chemical equilibrium.

Consider first the conversion at the temperature T of a mols of A, b mols of B, $\dots$ at pressures $p'_A, p'_B, \dots$ into e mols of E, f mols of F, $\dots$ at pressures $p'_E, p'_F, \dots$ by the gaseous reaction $aA + bB \dots = eE + fF \dots$. Let $p_A, p_B \dots p_E, p_F \dots$ be the partial pressures of A, B, $\dots$ E, F, $\dots$ in any one of the many possible mixtures of these gases which satisfy the equilibrium conditions of the reaction. Now, from free energy relations previously derived under the assumption of the laws of perfect gases, it follows that the last term ($-\Delta F$) in the free energy equation,

$$aA \text{ (at } p'_A) + bB \text{ (at } p'_B) \dots = eE \text{ (at } p'_E) + fF \text{ (at } p'_F) \dots - \Delta F,$$

may be obtained by summation of the following free energy equations:

$$aA \text{ (at } p'_A) = aA \text{ (at } p_A) + aRT \ln p'_A/p_A.$$

$$bB \text{ (at } p'_B) = bB \text{ (at } p_B) + bRT \ln p'_B/p_B.$$

$$aA \text{ (at } p_A) + bB \text{ (at } p_B) = eE \text{ (at } p_E) + fF \text{ (at } p_F) + 0.$$

$$eE \text{ (at } p_E) = eE \text{ (at } p'_E) + eRT \ln p_E/p'_E.$$

$$fF \text{ (at } p_F) = fF \text{ (at } p'_F) + fRT \ln p_F/p'_F.$$

The resulting expression for the free energy decrease ($-\Delta F$) may be written in the form:

$$-\Delta F = RT \ln \frac{p'_E p'_F \dots}{p'_A p'_B \dots} - RT \ln \frac{p_E p_F \dots}{p_A p_B \dots}. \quad (96a)$$

The first and third terms of the equation must have definite values determined by the change in state considered, and hence the ratio $(p'_E p'_F)/(p_A p_B)$ containing the partial pressures of A, B $\dots$ E, F $\dots$ in any equilibrium mixture must have a definite

value characteristic of the reaction and dependent only on the unit of pressure adopted. This, however, is a statement of the mass-action law as expressed by Eq. 92 (IV, 45).

For the special case that each gaseous reactant at the start and each gaseous reaction-product at the end is in its standard state (IV, 44) of 1 atm., the attendant free energy decrease $-\Delta F^\circ$ is expressed as follows:

$$-\Delta F^\circ = R T \ln K_p. \quad (96b)$$

By entirely analogous considerations the mass action-law, as expressed by Eq. 91 (a, b) (IV, 45), may be derived by deducing, under the assumption of the laws of perfect solutions, an expression for the free energy decrease attending each of the following changes in state in a liquid solution at the temperature T , and under an applied pressure of one atmosphere;

$$\begin{aligned} aA \text{ (at } c'_A) + bB \text{ (at } c'_B) \cdots &= eE \text{ (at } c'_E) + fF \text{ (at } c'_F) \cdots; \\ aA \text{ (at } X'_A) + bB \text{ (at } X'_B) \cdots &= eE \text{ (at } X'_E) + fF \text{ (at } X'_F) \cdots. \end{aligned}$$

The corresponding expressions are:

$$-\Delta F = R T \ln K_c - R T \ln \frac{c'^e_E c'^f_F \cdots}{c'^a_A c'^b_B \cdots}; \quad (97a)$$

$$-\Delta F = R T \ln K_X - R T \ln \frac{X'^e_E X'^f_F \cdots}{X'^a_A X'^b_B \cdots}. \quad (97b)$$

For the special case that each of the reactants at the start and each of the reaction-products at the end is in its standard state (IV, 44) of unit-activity, these expressions for the free energy decrease $-\Delta F^\circ$ attending the change take the forms:

$$-\Delta F^\circ = R T \ln K_c \quad (97c); \quad \text{or} \quad -\Delta F^\circ = R T \ln K_X. \quad (97d)$$

Equations 96 (a, b) and 97 (a, b, c, d), and hence also the corresponding expressions of the mass-action law (Eqs. 91 (a, b), 92), are inexact because of the assumption of the laws of perfect gases and perfect solutions. However, the fugacity or relative activity of any molecular species has been so defined (IV, 44) that errors due to such assumptions can be entirely eliminated from these equations by substituting fugacities for the partial pressure of gaseous species, and activities for the

weight-molalities or mol-fractions of dissolved species in the free energy equations employed in their derivation. For practical application this involves, of course, a knowledge of the corresponding activity-coefficients (or empirical correction factors) of the respective species. The resulting exact equations are:

$$-\Delta F = R T \left(\ln K_f - \ln \frac{p'_E p'_F \cdots}{p'_A p'_B \cdots} \times \frac{\alpha'_E \alpha'_F \cdots}{\alpha'_A \alpha'_B \cdots} \right), \quad (96c)$$

$$-\Delta F^\circ = R T \ln K_f, \quad (96d)$$

$$-\Delta F = R T \left(\ln K_a - \ln \frac{c'_E c'_F \cdots}{c'_A c'_B \cdots} \times \frac{\alpha'_E \alpha'_F \cdots}{\alpha'_A \alpha'_B \cdots} \right), \quad (97e)$$

$$-\Delta F^\circ = R T \ln K_a, \quad (97f)$$

$$-\Delta F = R T \left(\ln K_a - \ln \frac{X'_E X'_F \cdots}{X'_A X'_B \cdots} \times \frac{\alpha'_E \alpha'_F \cdots}{\alpha'_A \alpha'_B \cdots} \right), \quad (97g)$$

$$-\Delta F^\circ = R T \ln K_a. \quad (97h)$$

In these equations, $K_f = K_p(\alpha_E^\circ \alpha_F^\circ / \alpha_A^\circ \alpha_B^\circ)$; and

$$K_a = K_c(\alpha_E^\circ \alpha_F^\circ / \alpha_A^\circ \alpha_B^\circ); \quad \text{or} \quad K_a = K_X(\alpha_E^\circ \alpha_F^\circ / \alpha_A^\circ \alpha_B^\circ),$$

where $\alpha_A, \alpha_B \cdots \alpha_E, \alpha_F \cdots$ represent the activity-coefficients of the reactants and reaction-products in the actual equilibrium mixtures from which K_p, K_c , and K_X are computed. As the pressure on the gaseous solution, or the solute molalities and mol-fractions in the liquid solution (at constant pressure) approach zero, it is evident that the values of K_p, K_c , and K_X found by experiment approach as definite limiting values the corresponding true, or so-called *thermodynamic equilibrium constants* K_f and K_a of the reaction expressed in terms of fugacities or activities.

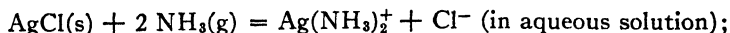
The free-energy increase ΔF° for the special case that each of the reactants at the start and each of the reaction-products at the end is in some specified standard state of unit activity is commonly called the *standard free energy of the reaction*. It is evidently a constant characteristic of the reaction, whose numerical value (like that of its equilibrium constant) is dependent only on the choice of the standard states.

The expression of the mass-action law in the form of Eqs. 93 (a, b) and 94, which do not depend either on the laws of perfect gases or those of perfect solutions, can be directly derived, as has already been indicated, from the broad criterion of equilibrium conditions expressed by Eq. 95, the concept of relative activity expressed by Eq. 85 (IV, 43), and the commonly adopted standard states of unit-activity of substances defined in an earlier article (IV, 44). The simplicity and brevity of this derivation are shown in the following problem. A comparison of this derivation with that carried out in the text demonstrates very clearly that activity-coefficients may be considered to be empirical factors introduced to eliminate the errors due to the assumptions of the laws of perfect gases and perfect solutes when the more usual expression of the mass-action law in the form of Eqs. 91 (a, b) and 92 is employed.

Prob. 72. — Derivation of the Mass-Action Law by Direct Use of the Concept of Activity. — a. Derive Eqs. 93 (a, b) and 94 from Eq. 95 with the aid of Eq. 85 (IV, 43) and the definitions of the standard states of unit-activity presented in IV, 44.

The illustrative example considered in Prob. 73 serves to show how the mass-action law of homogeneous chemical equilibrium can be extended to include all types of heterogeneous equilibrium. As already stated in the opening paragraph of this section, applications of the mass-action law in all of its forms will be fully treated in Chapter VII.

Prob. 73. — Form of the Mass-Action Law Applied to Heterogeneous Chemical Equilibrium. — a. By considerations similar to those of the preceding problem, derive an exact expression for the standard free energy ΔF° of the chemical change



and show that the equilibrium-constant of this reaction (which involves the activities of substances in three phases) is expressed by the equation,

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{f_{\text{NH}_3}^2} = \frac{(\text{Ag}(\text{NH}_3)_2^+)(\text{Cl}^-)}{p_{\text{NH}_3}^2} \times \frac{(\alpha_{\text{Ag}(\text{NH}_3)_2^+})(\alpha_{\text{Cl}^-})}{\alpha_{\text{NH}_3}^2}$$

b. With the aid of this mass-action expression, formulate an equation which shows how the formal solubility s of AgCl in water

saturated with ammonia gas at a pressure p_{NH_3} varies with that pressure. Practically all of the dissolved silver chloride is in the form of completely ionized $\text{Ag}(\text{NH}_3)_2^+ \text{Cl}^-$. Assume the laws of perfect gases and perfect solutions. *c.* At 25° an aqueous solution 0.1 wf. in NH_3 when saturated with silver chloride is 0.0044 wf. in AgCl . Calculate the weight-formal solubility of silver chloride in an aqueous solution 0.2 wf. in NH_3 , assuming that the dissolved ammonia conforms to Henry's law, and that the ions behave as perfect solutes. Note that the small proportion of the dissolved ammonia combined in the form of the complex cation $\text{Ag}(\text{NH}_3)_2^+$ may here be neglected without large error.



CHAPTER V

THE ELECTRICAL PROPERTIES OF SOLUTIONS AND THE IONIC THEORY

I. MOLAR EFFECTS OF IONIZED SUBSTANCES ON PROPERTIES OF SOLUTIONS. THE IONIC AND ION-ATTRACTION THEORIES.

1. Molar Effects of Salts in Aqueous Solutions and Their Explanation by the Ionic Theory. — At small concentrations the effect of salts of the uniunivalent type, such as potassium chloride or silver nitrate, on the vapor-pressure, freezing-point, or other related property of water is not far from twice as great, and the effect of salts of the unibivalent type, such as potassium sulfate and barium nitrate, is between two and three times as great as it would be if each formular weight of the salt yielded a single mol of a perfect solute. And as the concentration approaches zero, the value of this ratio approaches 2.00 for the uniunivalent salts, and 3.00 for the unibivalent. Strong acids and bases show a similar behavior.

The ratio of the experimentally found molar effect produced by one formular weight of any substance to that produced by one mol of a perfect solute is here called the *molar coefficient i* (*van't Hoff, 1886*) of the substance at the specified concentration.

To illustrate these statements, the effects at concentrations 0.005 to 0.05 weight-formal of some typical salts on the freezing-point of water are shown in Table I. The values given in the columns headed "Obs." are the molar coefficients derived from the measured freezing-point lowering (*I.C.T.*, 4, 254, 1928; *Randall, Scott, 1927*, for $\text{Ba}(\text{NO}_3)_2$ and Na_2SO_4) by dividing it by the weight-formality and by 1.859, which is the molal freezing-point lowering for water (*IV, 16*). The values given in the columns headed "Theor." have a significance which will be described below (*V, 6*).

These effects and certain electrical phenomena described below have led to the conclusion that salts, strong acids, and bases in aqueous solution are largely dissociated into electrically

TABLE I. MOLAR COEFFICIENTS OF SALTS CALCULATED FROM OBSERVED FREEZING-POINT LOWERINGS BY THE ION-ATTRACTION EQUATION.

Solute	0.005 Formal		0.010 Formal		0.020 Formal		0.050 Formal	
	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.
Uniunivalent								
HCl	1.956	1.946	1.940	1.926	1.920	1.894	1.90	1.83
KCl	1.963	"	1.941	"	1.921	"	1.89	"
KNO ₃	1.958	"	1.932	"	1.902	"	1.85	"
CsNO ₃	1.952	"	1.930	"	1.910	"	1.82	"
Unibivalent								
Na ₂ SO ₄	2.78	2.72	2.70	2.61	2.62	2.45	2.48	2.13
K ₂ SO ₄	2.77	"	2.70	"	2.60	"	2.45	"
Ba(NO ₃) ₂	2.76	"	2.67	"	2.56	"	2.39	"
Pb(NO ₃) ₂	2.74	"	2.68	"	2.51	"	2.30	"
Unitrivalent								
La(NO ₃) ₃	3.49	3.22	3.35	—	3.23	—	3.09	—
Bibivalent								
MgSO ₄	1.62	1.58	1.53	1.40	1.43	1.15	1.30	0.66

charged molecules or ions (*Arrhenius*, 1887); namely, into equivalent quantities of negative ions, also called *anions*, produced by combination of one or more electrons with neutral atoms or atom-groups, and of positive ions, also called *cations*, produced by removal of one or more electrons from neutral atoms or atom-groups (*I*, 5). The number of unit electric charges on an ion is called its *electrovalence*; this being positive in the case of proton-charges and negative in the case of electron-charges.

A striking principle shown by the observed values of the molar coefficients in Table I is that these values are nearly the same for different substances of the same electrovalence type, even though their chemical natures are as different as those of hydrogen chloride, potassium chloride and cesium nitrate, or as those of potassium sulfate, barium nitrate and lead nitrate. This clearly indicates that the decrease in the molar coefficient with increasing concentration arises in these cases, not from a molecular union of the ions that is caused as usual by specific chemical affinities, but either from a molecular union determined

by the electric charges on the ions or from molecule attraction arising from those charges (*Noyes, 1904*). It is also seen from Table I that the decrease in the molar coefficient below its limiting value is at a given formality much greater, the greater the product of the electrovalences and therefore the greater the product of the electric charges of the two ions — again indicating that the effect is of electrical origin.

2. Ionization of Substances Derived from Their Molar Coefficients. — The fraction of a solute that is dissociated into its ions is called its *ionization* γ . From the effects of salts upon the vapor-pressure, boiling-point, or freezing-point of water, or upon the osmotic pressure, their ionization was formerly commonly evaluated under the assumption that ions (and unionized molecules) act like perfect solutes. Thus the ionization was calculated from the molar coefficient corresponding to the observed effects by the equations:

$$i = (1 - \gamma) + 2\gamma = 1 + \gamma, \text{ for diionic solutes,} \quad (1)$$

$$i = (1 - \gamma) + 3\gamma = 1 + 2\gamma, \text{ for triionic solutes.} \quad (2)$$

For example, under this assumption the conclusion would be drawn from the data of Table I that in 0.05 weight-formal solution the ionization of potassium chloride is 89%, of potassium sulfate 73%, and of magnesium sulfate 30%.

Experimental evidence and theoretical considerations, however, have shown that ions influence these molar effects of aqueous solutions, even at small concentrations, such as 0.05 formal, much less than do an equal number of molecules of a perfect solute. These deviations make it unreliable to derive in this way even approximate ionization values for salts, even in dilute solutions. And quite without significance are estimates, based on the molar coefficient, as to the magnitude of the (small) fraction of the salt that exists in the unionized state. Indeed, there are strong indications that most salts and strong monobasic acids and bases are nearly completely ionized up to large concentrations, and that the observed decrease in the molar coefficients is due almost wholly to the fact that ions exert an increasingly small molar effect as their concentration increases.

The ratios of the molar effects of ions to those of perfect solutes are fully considered below (*V, 4*). The magnitudes of

these *molar coefficients of the ions* i^+ , i^- are illustrated at 0.005 to 0.05 formal, under the assumption of complete ionization, by the observed values of the molar coefficients of the salts given in Table I; which for diionic salts are twice and for triionic salts three times the average of the values for the two ions.

In spite of the large deviations of the molar effects of ions from those of perfect solutes, measurements of the molar coefficients of salts often throw much light on the nature of the ions existing in aqueous solutions and on the order of magnitude of their concentrations.

Prob. 1. — The Two Limiting Interpretations of the Molar Effects of Salts. — A solution of 0.65 KCl in 1000 g. of water has at 100° a vapor-pressure of 744.8 mm. *a.* Calculate the molar coefficient of the salt. *b.* Find the ionization of the salt to which this value would correspond, assuming that the ions and unionized molecules act as perfect solutes. *c.* Find the percentage deviation of the molar coefficient of each ion from that of a perfect solute, assuming that the ionization is complete and that the molar effects of the two ions are equal.

Prob. 2. — Complex-Ion Formation Derived from Freezing-Point. — A 0.137 wf. AgNO_3 solution freezes at -0.447° , a 0.4 wf. NH_3 solution at -0.744° , and a solution 0.137 wf. in AgNO_3 and 0.4 wf. in NH_3 freezes at -0.670° . In the last solution Ag^+ ion is present at extremely small concentration (as shown by its giving no precipitate of Ag_2O with the excess of NH_3), because the ion has been converted almost completely into a complex ion $\text{Ag}(\text{NH}_3)_n^+$. *a.* From the above freezing-point data determine the value of n in each molecule of the complex ion, assuming that the simple and complex ions have the same molar coefficients. *b.* State what the freezing-point of the solution of pure ammonia shows as to the state in which it exists in aqueous solution.

3. Basis of the Ion-Attraction Theory. — There may be outlined at once the essential features of a theory, known as the *ion-attraction theory* (Milner, 1912; Debye, Hückel, 1923), which explains the abnormally small molar effect of ions on the physical properties of solutions (as well as on chemical equilibria in solution), and which accounts for some of the phenomena of electrical conductance that are to be considered in this chapter.

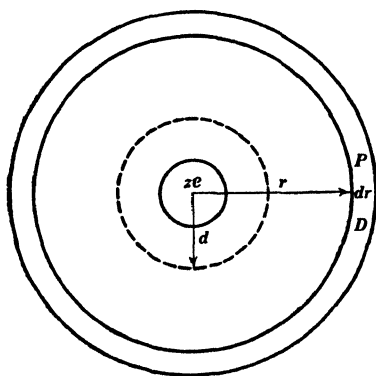
The fundamental ideas underlying this theory are as follows.

According to *Coulomb's law* there exists between any two elementary electric charges Q_1 and Q_2 a force f , which is one of repulsion when the charges are of like sign, and one of attraction when they are of unlike sign. This electric force is expressed by the following equation, in which l represents the distance between the charges and κ represents a constant, known as the *dielectric constant* of the medium, dependent on the nature, temperature, and pressure of the (homogeneous) medium separating the charges:

$$f = - \frac{Q_1 Q_2}{\kappa l^2}. \quad (3)$$

Consider now specifically, as illustrated in Fig. 1, a "selected" ion with a positive charge ze (represented by the

FIGURE 1. ION ATMOSPHERE.



central circle in the figure) in a solution containing free positive and negative ions, and consider the radial distance d (represented by the radius of the broken circle) to be the average distance of nearest approach of these ions to the selected ion. This distance is the apparent diameter of the ions (III, 16). The spherical shell between the selected ion and the other ions constitutes an ion-free (dielectric) medium separating the (positive) charge of the selected ion from the net equal (negative) charge of the other ions. The charge on the selected ion may be regarded as a point charge at its center. The equal charge of opposite sign is distributed non-uniformly, but with spherical symmetry, about

the sphere of radius d , as shown by the following considerations. This outer region of non-uniform distribution of electric charge is called the *ion-atmosphere*.

Consider (as represented by the space between the two outer circles) a spherical shell of thickness dr at a radial distance r from the selected ion. In this shell of infinitesimal volume the selected ion produces, as a result of its attraction for negative ions and repulsion of positive ions, a certain larger average concentration $\bar{n}_n, \bar{n}_r, \dots$ of each species of negative ion, and a certain smaller average concentration $\bar{n}_A, \bar{n}_B, \dots$ of each species of positive ion than the uniform concentrations $\bar{n}_{A0}, \bar{n}_{B0}, \bar{n}_{r0}, \dots$ that prevail at a large distance from the selected ion. Correspondingly, in this shell the selected ion produces a certain space density D of electric charge, and a certain potential P . In fact according to Boltzmann's equation (Eq. 39; III, 20) the produced concentration ratios $\bar{n}_A/\bar{n}_{A0}, \dots$ of the respective ion species in the shell are determined by the electrical energy of transfer of those species from the distance where uniform concentrations $\bar{n}_{A0}, \bar{n}_{B0}, \dots$ prevail into the spherical shell at the distance r . These increases in potential energy are equal to $P z_A e, \dots, P z_B e, \dots$, where $z_A, \dots, z_B, \dots$ are the (positive or negative) electrovalences of the ions.

In consequence of this non-uniform distribution of ions, there is a resultant attraction between any selected ion and all the ions in its neighborhood, so that in separating the ions from one another, as is done in diluting the solution with solvent, a force of attraction has to be overcome; whereas on diluting a perfect solution there is no such effect (IV, 38). Consequently, the maximum work (such as $NR T \ln (c_1/c_2)$) which the solution could otherwise yield upon dilution is diminished by an amount equal to the energy increase (because of ion-attraction) when the solution is diluted isothermally from its actual concentration c_1 to a concentration c_2 so small that ion-attraction is negligible. This diminution of the reversible work (and hence of the free energy) of dilution corresponds to a smaller osmotic pressure of the ions, and to a smaller change in the vapor-pressure, boiling-point, and freezing-point of the solvent than the ions would produce if they were perfect solutes (with no attraction between the molecules).

These conditions are analogous to those presented by perfect and imperfect gases. In a perfect gas the molecules exert no attraction upon one another, and no energy is required for their separation. On the other hand, in an imperfect gas there is an attraction between the molecules which must be overcome when they are separated, as is shown by the observed increase in energy-content of the gas when it expands isothermally (*III*, 32). And just as this attraction of the molecules for one another reduces the pressure of the gas below that of a perfect gas, so in the case of a solution of ions their resultant attraction for one another causes the ions to produce smaller osmotic pressure, and smaller molar effects in general than the ions would produce if they were perfect solutes.

4. Molar Coefficients of Salts and Ions Given by the Ion-Attraction Theory. — From the foregoing considerations, making use only of Boltzmann's equation, of Coulomb's law, and of other fundamental principles of electrostatics, there can be derived by mathematical processes (*V*, 7) a quantitative expression for the amount by which the reversible work of transfer of a completely ionized salt between two moderately dilute ion-containing solutions is reduced because of the non-uniform distribution of the ions, of their resultant attraction, and of the electrical energy expended in their separation. And from the free-energy decrease attending such transfer, thus corrected for the ion-attractions, there can be obtained the following expression, valid at small ion-concentrations, for the molar coefficient i (*V*, 1) of a salt of the type $A_n E$ (*Debye, Hückel, 1923*):

$$i = (1+a) \left[1 - 9.87 \times 10^8 \frac{z_n^2}{a (\kappa T)^{1.5}} (\Sigma c z^2)^{\frac{1}{2}} \right]. \quad (4)$$

In this expression z_n is the (positive or negative) electrovalence of the multivalent ion species E , while κ is the dielectric constant of the solvent referred to that of a vacuum as unity, and T is the absolute temperature. And the quantity $\Sigma (c z^2)$ denotes the sum, taken in general for all the species of ions (A , B , $\dots$, E , F , $\dots$) present, of the product $c z^2$ of the volume-molal concentration c of each ion-species by the square of its electrovalence z . That is:

$$\Sigma (c z^2) = c_A z_A^2 + c_B z_B^2 + \dots + c_n z_n^2 + c_r z_r^2 + \dots \quad (5)$$

As this summated quantity determines the effect of ionic attraction in its various applications, it would be convenient to have a name for it; but it is customary, instead, to employ a name for one-half of its value, namely, for the quantity $\frac{1}{2} \Sigma (c z^2)$, which had been previously called the *ionic strength* μ of the solution (Lewis, Randall, 1921). The quantity 2μ actually occurring in the ion-attraction formulas may be called the *double ion-strength*. Evidently the double ion-strength of a single uniunivalent salt is equal to twice its volume-formal concentration; while that of a single bibivalent salt is eight times, and that of a single unibivalent salt is six times, its volume-formal concentration.

The above expression (Eq. 4) for the molar coefficient i of a salt is approximately exact only at very small double ion-strengths (such as 0.04 molal) for the reason that in its derivation an effect due to the size of the ion was neglected and that certain mathematical approximations were introduced.

For the solvent water at 0° and at 25° , where its dielectric constant is 88.0 and 78.0, respectively (I.C.T., 6, 78; $\kappa = 88 - 0.40 t$), Eq. 4 becomes for a salt $A_a E$:

$$i = (1+a) [1 - 0.264 (z_a^2/a) (\Sigma c z^2)^{\frac{1}{2}}], \text{ in water at } 0^\circ, \quad (6)$$

$$i = (1+a) [1 - 0.278 (z_a^2/a) (\Sigma c z^2)^{\frac{1}{2}}], \text{ in water at } 25^\circ. \quad (7)$$

The total molar effect on the vapor-pressure or freezing-point lowering of the solvent or on the osmotic pressure of a solution is found by multiplying in the perfect-solution formulas the formal mol-fraction or mol-ratio or formal concentration of the salt by its molar coefficient i calculated as just described.

There can be derived by similar considerations the following expressions, valid at small ionic strengths, for the molar coefficient i_A of any ion species A with electrovalence z_A :

$$i_A = 1 - 9.87 \times 10^5 z_A^2 \sqrt{\Sigma (c z^2)} / (\kappa T)^{1.5}, \quad (8)$$

$$i_A = 1 - 0.264 z_A^2 \sqrt{\Sigma (c z^2)}, \text{ in water at } 0^\circ, \quad (9)$$

$$i_A = 1 - 0.278 z_A^2 \sqrt{\Sigma (c z^2)}, \text{ in water at } 25^\circ. \quad (10)$$

It will be seen from these equations that the molar coefficient of a given species of ion (at small ionic strengths) is deter-

mined by no other property of that ion than its electric charge; and therefore that its value is equal for different species of ion with the same charge, equal also whether that charge is positive or negative (since the electrovalence enters as the square). It will also be seen that the molar coefficient of any given ion species decreases (from unity at ionic strength zero) proportionally to the square-root of the ionic strength, so that it diminishes when the total concentration or the electrovalence of the ions in the solution increases.

5. Molar Effects Derived from the Ion-Attraction Theory of Completely Ionized Solutes on the Properties of Solvents. —

The total molar effect on a solvent predicted by the theory for a completely ionized salt or a mixture of them is found by summing the separate effects of the various species of ion present; these separate effects being determined by multiplying in the perfect-solution formulas the mol-fraction or mol-ratio of each ion-species by its molar coefficient calculated as just described. Thus the vapor-pressure lowering or freezing-point lowering of a solvent or the osmotic pressure of a solution caused by ions A, B, ..., E, F, ... (caused, for example, by a solution of potassium sulfate and magnesium nitrate) present at mol-fractions $X_A, X_B, \dots, X_E, X_F, \dots$ or at mol-ratios $N_A/N_0, \dots, N_E/N_0, \dots$ would be expressed by the equations:

$$(p_0 - p)/p_0 = X_A i_A + X_B i_B + \dots + X_E i_E + X_F i_F + \dots, \quad (11)$$

$$T_0 - T = \frac{R T_0^2}{\Delta \tilde{H}_F} \left[\frac{N_A i_A}{N_0} + \dots + \frac{N_E i_E}{N_0} + \dots \right], \quad (12)$$

$$T_0 - T = 1.859 (c_A i_A + \dots + c_E i_E + \dots), \text{ in water solution, } \quad (13)$$

$$P v = R T (N_A i_A + \dots + N_E i_E + \dots). \quad (14)$$

It is to be noted, however, that these molar coefficients can not be applied in the same way as activity-coefficients (IV, 44) in determining the properties of solutes, such as their vapor-pressure in connection with Henry's law, or their concentration in connection with distribution between liquid phases or with chemical equilibrium. The form which these corrections take will be considered later (V, 7).

Prob. 3. — Freezing-Point Lowering by a Completely Ionized Triionic Salt Derived from the Ion-Attraction Theory. — Formulate an expression with numerical coefficients for the freezing-point lowering $T_0 - T$ of a c wf. aqueous solution of potassium sulfate, assuming the salt to be completely ionized and to conform to the dilute-solution ion-attraction equation.

Prob. 4. — Molar Coefficient of a Salt in Relation to the Molar Coefficients of Its Ions. — Derive the expression (Eq. 4) for the molar coefficient of a salt $A_a E$ from the corresponding expressions (Eq. 8) for those of its separate ions, noting that $i = (a i_A + i_E)$.

**** Prob. 5. — Secondary Ionization of Sulfuric Acid Derived from Its Freezing-Point by the Ion-Attraction Theory.** — Considering the primary ionization of sulfuric acid to be complete (that is, that all H_2SO_4 is ionized into H^+ and HSO_4^-), evaluate its secondary ionization γ_2 (that of HSO_4^- into H^+ and SO_4^{--}), with the aid of the dilute-solution ion-attraction equation, by proceeding as follows:

a. Make a preliminary estimate of the double ion-strength $\Sigma (c z^2)$ in a 0.010 wf. H_2SO_4 solution under the provisional assumption that the secondary ionization has the midway value of 50%.

b. Using this ionization value and the freezing-point of 0.01 wf. H_2SO_4 which is -0.04584° , set up a numerical ion-attraction equation involving the secondary ionization γ_2 , and solve it for this quantity. *Ans.* γ_2 , 0.725.

c. Using this ionization value make a new estimate of the double ion-strength in a 0.010 wf. H_2SO_4 solution.

d. From the new double ion-strength and the freezing-point -0.04584° , calculate a new value of the secondary ionization γ_2 . *Ans.* γ_2 , 0.761.

6. Validity of Ion-Attraction Theory in Dilute Solution.

— The adequacy of the ion-attraction theory is shown in Table I (*V, 1*) by the degree of conformity of the "theoretical" values of the molar coefficients i of salts calculated by the dilute-solution ion-attraction equation (Eq. 6) with the "observed" values obtained by dividing the measured freezing-points by the formality and by 1.859 (the molal freezing-point lowering for water), for various substances of three electrovalence types at 0.005, 0.01, 0.02, and 0.05 weight-formal.

These results justify the following conclusions.

(1) The observed molar coefficients are, as the ion-attraction theory requires, nearly identical for different salts of the same

electrovalence type at small concentrations, namely, up to about 0.020 formal for uniunivalent salts, and up to about 0.005 formal for unibivalent salts; but differ considerably from one another at higher concentrations.

(2) The theoretical values of the molar coefficients agree fairly closely with the observed values up to about 0.020 formal in the case of uniunivalent salts, but only up to about 0.005 formal in the case of unibivalent and bibivalent salts. More generally expressed, the dilute-solution ion-attraction equation expresses the actual results fairly closely (within 1 to 3%) for salts of all electrovalence types up to an ionic strength of 0.02 molal.*

(3) Even at ionic strengths no larger than 0.10 and 0.20 molal the ion-attraction equation gives values that deviate very largely in the case of unibivalent and bibivalent salts; thus the deviations for barium nitrate and for potassium and sodium sulfates are 12–16% at ionic strength 0.15 molal (concentration, 0.05 wf.). These deviations arise, as above stated, at least in part from the fact that in the derivation of the dilute-solution ion-attraction equation the effect of the size of the ion was neglected and certain mathematical approximations were made.

The close agreement at small concentrations of the observed freezing-point lowerings with those predicted by the ion-attraction theory under the assumption of complete ionization is evidence of the correctness of this assumption at such concentrations. This assumption is further supported by the fact that at larger concentrations the observed freezing-point lowerings are not smaller, but larger, than those predicted, the effect being in the direction opposite to that which incomplete ionization would produce.

**** 7. Derivation of the Ion-Attraction Equations.** — The derivation of the ion-attraction equations (*Debye, Hückel, 1923*) includes a series of steps, in which a number of separate mathematico-physical principles are involved. Referring to the previous articles and to Fig. 1 (*V, 3*) for the underlying conceptions and the notation, and considering a solution which at temperature

* The univalent salt, lanthanum nitrate, shows a considerable deviation even at its smallest concentration, 0.005 formal; but this corresponds already to an ionic strength of 0.03 molal. At the higher concentrations the deviations of the dilute-solution equation are so large as to make the calculated molar coefficient of the lanthanum ion negative.

T contains on an average per cubic centimeter $\bar{n}_{A0}, \bar{n}_{B0}, \dots, \bar{n}_{E0}, \bar{n}_{F0}, \dots$ ion-molecules of the ion-species A, B, $\dots$, E, F, $\dots$ with respective positive or negative charges $z_A e, z_B e, \dots, z_E e, z_F e, \dots$, these steps may be outlined as follows:

(1) *Ion-Concentration Ratios $\bar{n}_A/\bar{n}_{A0}, \dots, \bar{n}_E/\bar{n}_{E0}, \dots$ at Radial Distance r from a Selected Positive Ion.* — By substituting in separate Boltzmann's equations (Eq. 39; III, 20) for the potential energy E^P the quantities $P z_A e, \dots, P z_E e, \dots$ of energy absorbed in transferring a single ion of the various species from the distance r , where a potential P prevails, to an infinite distance from the selected ion, there are found the following expressions for the ion-concentrations in the shell dr :

$$\bar{n}_A = \bar{n}_{A0} e^{-(P z_A e / kT)}; \dots; \bar{n}_E = \bar{n}_{E0} e^{-(P z_E e / kT)}; \dots \quad (15)$$

Developing the exponential factors into a series, and retaining only the first two terms, these expressions become:

$$\bar{n}_A = \bar{n}_{A0} \left(1 - \frac{P e z_A}{k T} \right); \dots; \bar{n}_E = \bar{n}_{E0} \left(1 - \frac{P e z_E}{k T} \right); \dots \quad (16)$$

(2) *Electric Density D of the Ion-Atmosphere at Distance r from a Selected Ion.* — The electric density of ionic charge may evidently be obtained by multiplying by its respective charge $z_A e, \dots, z_E e, \dots$ the concentration $\bar{n}_A, \bar{n}_E, \dots$ of each species of ion as expressed by Eq. 16 and summing the resulting products algebraically. Noting also that $\bar{n}_{A0} z_A + \bar{n}_{B0} z_B + \dots + \bar{n}_{E0} z_E + \bar{n}_{F0} z_F + \dots = 0$, since the average numbers of equivalents of positive and negative ions are equal, it follows that:

$$D = - \frac{e^2 P}{k T} (\bar{n}_{A0} z_A^2 + \bar{n}_{B0} z_B^2 + \dots + \bar{n}_{E0} z_E^2 + \bar{n}_{F0} z_F^2 + \dots); \quad \text{or}$$

$$D = - \frac{e^2 P}{k T} \Sigma (\bar{n}_0 z^2). \quad (17)$$

(3) *Potential P at Distance r from a Selected Ion in Relation to the Resultant Density D of the Ion-Atmosphere.* — By Coulomb's law (V, §) it can be shown that in an ion-containing medium of dielectric constant κ surrounding a selected ion the potential P must fall off symmetrically with the radial distance r and the resultant space charge D in accord with the following differential equation, known as Poisson's equation:

$$\frac{d^2 P}{dr^2} + \frac{2}{r} \frac{dP}{dr} + \frac{4 \pi D}{\kappa} = 0. \quad (18)$$

Replacement of the density D by the expression given for it in Eq. 17 yields:

$$\frac{d^2 P}{dr^2} + \frac{2}{r} \frac{dP}{dr} - \frac{4 \pi e^2 \Sigma (\bar{n}_0 z^2)}{K k T} P = 0. \quad (19)$$

On writing the simpler symbol B^2 for the P coefficient, which is constant with respect to variation of the distance r , there results:

$$\frac{d^2 P}{dr^2} + \frac{2}{r} \frac{dP}{dr} - B^2 P = 0. \quad (20)$$

This equation leads to the following indefinite integral, in which I and I' are the two integration constants:

$$P = I \frac{e^{-Br}}{r} + I' \frac{e^{Br}}{r}. \quad (21)$$

In the case here considered the integration constant I' must have the value zero, since otherwise the potential calculated by Eq. 21 would become infinite as the distance r approaches infinity. Noting this simplification of the equation, its differentiation with respect to r yields the following expression for the potential gradient $-dP/dr$ (or field strength) in the ion-atmosphere at the distance r :

$$-\frac{dP}{dr} = \frac{I(1+Br)}{r^2} e^{-Br}. \quad (22)$$

This equation is valid for values of r greater than the apparent diameter d of the ions ($V, 3$; Fig. 1). For values of r less than d the potential gradient is determined by the charge on the selected ion, and is expressed by the equation:

$$-\frac{dP}{dr} = \frac{ze}{K r^2}. \quad (23)$$

At the unique distance where r is equal to d there thus exist two independent equations for the potential gradient. By substitution of d for r in the two equations, and equating the results, there is obtained the following expression for the integration constant I :

$$I = \frac{ze}{K} \left(\frac{e^{Bd}}{1+Bd} \right). \quad (24a)$$

Substitution in Eq. 21 of these values of I and I' results in the following expression for the potential P in the ion-atmos-

phere at any distance r from the selected ion of charge ze :

$$P = \frac{ze}{K r} \left(\frac{e^{Bd}}{1+Bd} \right) e^{-Br}, \quad \text{where} \quad B = \frac{2 \pi^{0.5} e (\Sigma \bar{n}_0 z^2)^{0.5}}{(K k T)^{0.5}}. \quad (25a)$$

This potential can, however, be resolved into two terms as follows:

$$P = \frac{ze}{K r} - \frac{ze}{K r} \left[1 - \left(\frac{e^{Bd}}{1+Bd} \right) e^{-Br} \right]. \quad (26a)$$

The first term is evidently the potential which the selected ion of charge ze would produce at the distance r in an ion-free medium; and the second term, which will be represented by P_{0d} , is, therefore, the potential in the shell at the distance r which corresponds to the space-charge or ion-atmosphere. At the surface of the ion itself, where r becomes equal to d , the potential P_{0d} , insofar as it is determined by the ion-atmosphere, is therefore:

$$P_{0d} = - \frac{ze}{K d} \left(\frac{Bd}{1+Bd} \right). \quad (27a)$$

As the ionic-strength, and therefore B , approaches zero, the factor $e^{Bd}/(1+Bd)$ occurring in Eqs. 24a, 25a, and 26a approaches unity, and the factor $Bd/(1+Bd)$ in Eq. 27a approaches the value Bd . Hence for solutions of small ionic-strength, these four equations may be written in the approximate forms:

$$I = \frac{ze}{K}, \quad (24b)$$

$$P = \frac{ze}{K r} e^{-Br}, \quad (25b)$$

$$P = \frac{ze}{K r} - \frac{ze}{K r} (1 - e^{-Br}), \quad (26b)$$

$$P_{0d} = - \frac{ze}{K} B. \quad (27b)$$

The further development of the ion-attraction theory which is here presented is based on these limiting equations; and the expressions derived from them are accordingly applicable without considerable error only to solutions of small ionic-strength.

(4) *Energy-Increments δE_A and $\Delta \tilde{E}_A$ That Attend the Removal of the Charge from a Selected Ion A and of the Charges from One Mol or $\bar{n}$ Molecules of a Selected Ion-Species A.*—From the general electrostatic principle that the building up of a charge Q to a potential P requires the expenditure of electrical energy $\frac{1}{2} P Q$ it follows (assuming an equivalent number of molecules of the ion-species of opposite charge to be discharged at the same time)

that these energy increments are:

$$\delta E_A = \frac{z_A^2 e^2 B}{2 K}, \quad (28)$$

$$\Delta E_A = \frac{z_A^2 e^2 B}{2 K} \tilde{n} = \frac{\pi^{0.5} e^3 \tilde{n} z_A^2 (\sum \bar{n}_0 z^2)^{0.5}}{k^{0.5} (K^3 T)^{0.5}}. \quad (29)$$

By replacement of $\bar{n}_0$ (ion-molecules per cubic centimeter) by c_0 (mols per liter), noting that $\bar{n}_0 = c_0 \tilde{n}/10^3$ where $\tilde{n}$ is Avogadro's number, there results:

$$\Delta \tilde{E}_A = \frac{\pi^{0.5} e^3 \tilde{n}^{1.5} z_A^2 (\sum c_0 z^2)^{0.5}}{(10^3 k)^{0.5} (K^3 T)^{0.5}}. \quad (30)$$

By consolidation of the universal constants into a single constant G there is obtained the equation:

$$\Delta \tilde{E}_A = G \frac{z_A^2 (\sum c_0 z^2)^{0.5}}{(K^3 T)^{0.5}} \text{ ergs,}$$

where

$$G = \frac{\pi^{0.5} e^3 \tilde{n}^{1.5}}{(10^3 k)^{0.5}} = 2.461 \times 10^{14}. \quad (31)$$

(5) *Electrical Work dE Producing by the Transfer of One Formular Weight of a Salt of Formula A_aE.*—To find the electrical work dE producible by the transfer of one formular weight of a salt A_aE from an infinite volume of its c formal solution to an infinite volume of its $c + dc$ formal solution, we consider the transfer made in the form of its two ions. One mol of E ion is transferred from its concentration c_E to its concentration $c_E + dc_E$, and a mols of A ion from its concentration c_A (equal to $a c_E$) to its concentration $c_A + dc_A$ (equal to $a c_E + a dc_E$). These transfers will occur between solutions whose double ion-strengths are $c_E z_E^2 + c_A z_A^2$ and $(c_E + dc_E) z_E^2 + (c_A + dc_A) z_A^2$, respectively, where z_E and z_A are the electrovalences of the two ions; and, since $z_A = z_E/a$, these double ion-strengths are equal to $z_E^2 c_E (1+a)/a$ and $z_E^2 (c_E + dc_E)(1+a)/a$, respectively. The electrical work producible by the transfer of the two ions (one mol of E and a mols of A) will therefore be given by the sum of two equations like Eq. 31—namely, by the expression:

$$dE = - \frac{G}{(K^3 T)^{0.5}} (z_E^2 + a z_A^2) d(\sum c_0 z^2)^{0.5}, \quad (32)$$

$$dE = - \frac{G z_E^2}{(K^3 T)^{0.5}} \frac{1+a}{a} d\left(c_E z_E^2 \frac{1+a}{a}\right)^{0.5}, \quad (33)$$

$$dE = - \frac{G z_E^3}{(K^3 T)^{0.5}} \left(\frac{1+a}{a}\right)^{1.5} \frac{dc_E}{2 c_E^{0.5}}. \quad (34)$$

(6) *Osmotic Pressure P of a Single Salt of Formula $A_a E$ Taking Account of the Ion-Attraction.*—An expression for the actual osmotic pressure P of the salt can be derived by considering the quantities of work attending the reversible transfer of one formular weight of $A_a E$ of the salt from an infinite volume of its c formal solution to an infinite volume of its $c + dc$ formal solution. Empirically the work attending this transfer is given in terms of the actual osmotic pressure P by the expression $\tilde{v} dP$, where $\tilde{v}$ denotes the volume of solution in which one formular weight of salt is present.* This actual work of transfer must be equal to the work of transfer of the salt in the form of its two ions; and this must be less than the perfect-solution work of transfer of the two ions by the electrical work attending their transfer between the two solutions. An expression for this electrical work has already been derived in Eq. 34. Noting that $\tilde{v}$ is equal to $1/c$ or $1/c_{\pm}$, and that the perfect-solution osmotic work in transferring a mols of ion A from c_A to $c_A + dc_A$ (or from $a c_{\pm}$ to $a c_{\pm} + a dc_{\pm}$) is $a R T dc_{\pm}/c_{\pm}$ and that the work in transferring one mol of ion E from c_E to $c_E + dc_E$ is $R T dc_E/c_E$, these relations may be expressed by the equations:

$$\frac{dP}{c_{\pm}} = (1+a) R T dc_{\pm}/c_{\pm} - \frac{G z_{\pm}^2}{(K^3 T)^{0.5}} \left(\frac{1+a}{a} \right)^{1.5} \frac{dc_{\pm}}{2 c_{\pm}^{0.5}}; \quad (35)$$

or

$$dP = (1+a) R T dc_{\pm} - \frac{G z_{\pm}^2}{2 (K^3 T)^{0.5}} \left(\frac{1+a}{a} \right)^{1.5} c_{\pm}^{0.5} dc_{\pm}. \quad (36)$$

Integration of this equation between the pressure limits P_0 and P and concentration limits $c_{\pm 0}$ and $c_{\pm}$ gives:

$$\frac{P - P_0}{1+a} = c_{\pm} R T - c_{\pm 0} R T - \frac{G z_{\pm}^2}{3 (K^3 T)^{0.5}} \frac{(1+a)^{0.5}}{a^{1.5}} (c_{\pm}^{1.5} - c_{\pm 0}^{1.5}). \quad (37)$$

In case $c_{\pm 0}$ is so small that ion-attraction is negligible, $P_0/(1+a)$ equals $c_{\pm 0} R T$ and the $c_{\pm 0}$ term in the ion-attraction work vanishes, so that this equation becomes:

$$\frac{P}{1+a} = c_{\pm} R T - \frac{G z_{\pm}^2}{3 (K^3 T)^{0.5}} \frac{(1+a)^{0.5}}{a^{1.5}} c_{\pm}^{1.5}. \quad (38)$$

(7) *Final Expression for the Osmotic Pressure.*—Writing the volume-formality c of the salt in place of the concentration $c_{\pm}$ of its multivalent ion E, there is finally obtained the following

* Although the osmotic work of dilution is $P d\tilde{v}$, the osmotic work of transfer of a solute between two solutions can be shown to be $\tilde{v} dP$, as here stated.

expression for the osmotic pressure P (in the units in which the gas-constant R is expressed) of a completely ionized salt of type $A_a E$ at centigrade temperature T , at that volume-formality, in a solvent of dielectric constant κ :

$$P = (1+a) c R T \left(1 - \frac{G}{3R} \frac{z_{\pm}^2 c^{0.5}}{(\kappa T)^{1.5}} \frac{(1+a)^{0.5}}{a^{1.5}} \right) \quad (39)$$

where

$$G/3R = 9.87 \times 10^6.$$

Noting that $\Sigma c z^2 = c z_{\pm}^2 (1+a)/a$, this may be readily shown to correspond to the molar coefficient i of a salt of the formula $A_a E$ as expressed by Eq. 4 (V, 4).

(8) *The Activity Coefficient α_A of an Ion A of Electrovalence z_A .* — It has already been pointed out (in deriving Eq. 38) that the work attending the reversible transfer of 1 mol of an ion A of electrovalence z_A from an infinite volume of its c_A molal solution to an infinite volume of its $c_A + dc_A$ molal solution is less than the perfect-solution work of transfer by the electrical work attending its transfer between the two solutions. It follows from Eq. 31 that the electrical work dE producible by such transfer is given by the equation:

$$dE = - \frac{G}{(\kappa^3 T)^{0.5}} z_A^2 d(\Sigma c_0 z^2)^{0.5}. \quad (40)$$

The corresponding expression for the molar free energy decrease $-d\tilde{F}_A$ is, accordingly,

$$-d\tilde{F}_A = -R T d \ln c_A + \frac{G}{(\kappa^3 T)^{0.5}} z_A^2 d(\Sigma c_0 z^2)^{0.5}. \quad (41)$$

Another expression for this molar free energy decrease in terms of the molal concentration c_A of the ion A and of its activity coefficient α_A may be derived by considering the activity of A (IV, 43) in relation to its partial molar free energy. This second expression is:

$$-d\tilde{F}_A = -R T d \ln c_A - R T d \ln \alpha_A. \quad (42)$$

By combining the last two equations there results:

$$d \ln \alpha_A = - \frac{G/R}{(\kappa T)^{1.5}} z_A^2 d(\Sigma c_0 z^2)^{0.5}. \quad (43)$$

This equation when integrated between the double ion-strength limits, 0 and $\Sigma (c_0 z^2)$, leads to the following expression:

$$\ln \alpha_A = - \frac{G/R}{(\kappa T)^{1.5}} z_A^2 \sqrt{\Sigma (c_0 z^2)} \quad (44)$$

where,

$$G/R = 2.96 \times 10^6.$$

It is often convenient to solve this equation for the common logarithm of the activity-coefficient, and to introduce the ionic strength μ (equal to $0.5 \sum c z^2$) of the solution into the final expression. Thus, for the solvent water at 25° , where its dielectric constant is 78.0, Eq. 44 takes the simple form:

$$\log \alpha_{\Delta} = -0.505 z_{\Delta}^2 \sqrt{\mu}. \quad (45)$$

This limiting ion-attraction equation becomes seriously inexact even at moderate ionic strengths because in its derivation certain mathematical approximations involving the apparent diameter d of the ion (shown in Figure 1 as the average distance of nearest approach of other ions to the selected ion) were introduced. Elimination of such approximations leads to a modified equation of the following form:

$$\log \alpha_{\Delta} = -\frac{0.61 G/R}{(\kappa T)^{1.5}} z_{\Delta}^2 \frac{\sqrt{\mu}}{1 + D_{\Delta} \sqrt{\mu}};$$

or

$$\log \alpha_{\Delta} = -0.505 z_{\Delta}^2 \frac{\sqrt{\mu}}{1 + D_{\Delta} \sqrt{\mu}} \text{ (for water at } 25^\circ\text{)}. \quad (46)$$

In these equations D_{Δ} is an empirical constant characteristic of the ion and the solvent at the specified temperature. Theoretically interpreted, $1 + D_{\Delta} \sqrt{\mu}$ is identical with $1 + B d$ occurring in Eq. 24a.

This modified dilute solution ion-attraction equation is, however, still inexact due to certain other assumptions which were involved in its derivation. Namely, it was assumed that the dielectric constant is not affected by the ions and is independent of their concentrations, and that there are no other causes for deviations from the laws of ideal solutions, such as those responsible for the salting out of non-electrolytes (IV, 28) or for the deviations from Raoult's law in the case of solutions of non-electrolytes (IV, 36). A more detailed consideration,* which can not be presented here, makes it advisable to formulate the ionic strength in terms of concentrations of the different ion-species expressed as mols per liter of solvent (instead of mols per liter of solution). In water solutions this is practically equivalent to evaluating the ionic strength from weight-molalities of the ion-species. When this is done, and the deviations due to the causes just mentioned are neglected, the average value of D_{Δ} at 25° for a

* See Scatchard, *Chem. Review*, 19, 309, 1936.

large number of ions has been found to be approximately equal to unity, and accordingly the modified dilute solution ion-attraction equation takes the simpler form:

$$\log \alpha_{\pm} = - 0.505 z_{\pm}^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \text{ (for water at } 25^{\circ}\text{).} \quad (47)$$

In a later chapter (VII, 6) a comparison is made of ion-activity-coefficients calculated by Eqs. 45 and 47 with those obtained by various experimental methods. Such a comparison shows that Eq. 45 is limited in its applications to solutions of very low ionic strength, whereas Eq. 47 holds closely up to ionic strengths of about 0.1 weight-molal, and often without large error up to ionic strengths of about 1 weight-molal.

II. CHEMICAL CHANGES AT THE ELECTRODES IN
ELECTROLYTIC AND VOLTAIC CELLS.

FARADAY'S LAW.

8. Electrolytic Conduction in General. — Conductors are divided into two classes with reference to the changes that are produced in them by the passage of electric currents. Those which undergo no chemical changes, but only a rise in temperature, are called *metallic conductors*. Those in which the passage of a current is attended by a chemical change are called *electrolytes*. Salts, bases, and acids in aqueous solution, and melted salts at high temperatures, are the most important classes of well-conducting electrolytes. The most obvious chemical changes attending the passage of a current through an electrolyte are those that take place at the surfaces of the metallic conductors where the current enters and leaves the electrolyte. The production of such chemical changes by a current resulting from an externally applied electromotive force is called *electrolysis*. The occurrence of such changes, when they themselves give rise to an electromotive force and an electric current, is called *voltaic action*. And correspondingly, the term *electrolytic cell* or *voltaic cell* denotes an arrangement in which electrolysis or voltaic action takes place (*II, 18*). Those portions of the metallic conductors that are in contact with the electrolyte are called the *electrodes*; the one at which the current leaves the electrolyte, or the one towards which the positive electricity flows through the electrolyte, is designated the *cathode*; the other, the *anode*.

9. Chemical Changes at the Electrodes: Qualitative Effects. — The total amount of chemical change produced at each electrode of an electrolytic or voltaic cell is fully determined by a simple, exact, fundamental law (Faraday's law; *II, 18; V, 10*). The nature of the substances produced is, however, dependent not only upon the chemical character of the cell, but also, in the case of a given cell, often upon a variety of physical conditions, such as temperature, current-density, applied electromotive force, and electrode-polarization. These phenomena will be fully considered later. At this point it will suffice to state in a general way the chemical principles underlying the so-called electromotive series of the elements, and then to illustrate by

concrete examples the products of electrolysis commonly resulting in a number of typical cells.

The *electromotive series* of the metals is a series in which the metals are arranged in the order in which they produce a decreasing electromotive force when set up as voltaic cells consisting of a metal and of a 1-molal solution of its ion as one half-cell, and consisting of hydrogen gas at one atmosphere in contact with platinum (or other inert metal) and with a 1-molal solution of hydrogen-ion as the other, reference half-cell. The value of the electromotive force which such a cell produces is called the *molal electrode potential* E° or *molal reduction potential* of the metal-metal-ion half-cell. For example, in the case of zinc, a cell is set up which may be formulated as follows: $\text{Zn(s)}, \text{Zn}^{++} (1 \text{ m.}) / \text{H}^+ (1 \text{ m.}), \text{H}_2 (1 \text{ atm.}) + \text{Pt}$; and, since it is found to have at 25° an electromotive force of $+0.758$ volt (positive in the direction in which the cell is written) the electrode potential of $\text{Zn(s)}, \text{Zn}^{++}$ at 25° is said to be $+0.758$ volt. Oxidizing combinations other than metals may be similarly treated; thus the electrode-potential of $\text{Cl}^- (1 \text{ m.}), \text{Cl}_2 (1 \text{ atm.})$ at 25° is -1.359 volts. The conventions involved in electrode-potentials and their experimental determination will be fully considered later.

It is to be noted that the actual electrode-potential is determined, not only by the nature of the metal, but also by the concentration of its ion: at 25° for every ten-fold decrease of the ion-concentration it decreases from the molal value by about 0.06 volt for a univalent ion, 0.03 volt for a bivalent ion, and 0.02 volt for a trivalent ion.

For purposes of illustration a partial list of the well-known molal electrode-potentials is given in Table II.

In determining the products of electrolysis the electrode-potentials are a factor of much importance; for the sum of two of these potentials corresponds to the minimum electromotive force that suffices to set free specified substances upon the two electrodes of an electrolytic cell. Thus, to set free at 25° tin and chlorine from a solution 1 m. in Sn^{++} and 1 m. in Cl^- , an electromotive force of at least 1.495 (equal to $0.136 + 1.359$) volt must be applied to the solution. When a considerably smaller electromotive force is applied hydrogen and oxygen, requiring only 1.22 volts, are set free. And when a larger one is applied

TABLE II. MOLAL ELECTRODE-POTENTIALS AT 25°.

<i>Reduced State</i>	<i>Oxidized State</i>	<i>Electrode-Potential</i>
K	K ⁺	2.922
Na	Na ⁺	2.713
Zn	Zn ⁺⁺	0.758
Fe	Fe ⁺⁺	0.441
Cd	Cd ⁺⁺	0.398
Tl	Tl ⁺	0.336
Sn	Sn ⁺⁺	0.136
Pb	Pb ⁺⁺	0.122
H ₂ (1 atm.)	2H ⁺	0.000
Cu	Cu ⁺⁺	-0.345
Cu	Cu ⁺	-0.47
I ⁻	$\frac{1}{2}$ I ₂ (s)	-0.536
Hg(l)	$\frac{1}{2}$ Hg ₂ ⁺⁺	-0.799
Ag	Ag ⁺	-0.800
Br ⁻	$\frac{1}{2}$ Br ₂ (1 m.)	-1.085
H ⁺ (1 m.) + H ₂ O(l)	O ₂ (1 atm.)	-1.22
Cl ⁻	$\frac{1}{2}$ Cl ₂ (1 atm.)	-1.359

all four of these products result, in proportions varying according to the conditions of electrolysis. The electrode-potentials afford therefore only an indication of what can or may happen.

Table III exemplifies types of chemical changes frequently occurring in electrolysis. It shows the products resulting when aqueous solutions of certain salts, bases, and acids are electrolysed between electrodes which are unattacked, for example, between platinum or carbon electrodes.

The results presented in Table III may be stated in more general form as follows:

(1) Acids, unless the anion is reducible, yield only hydrogen (cells 1, 2) at the cathode.

(2) Salts of copper (cell 3), bismuth, and antimony, and those of the so-called *noble metals*, silver, mercury, gold, and the platinum elements give cathode deposits of the metals; for the ions of these elements are so much more readily reduced than that of hydrogen that they are alone deposited on the cathode, even from solutions containing them at small concentrations and containing also much acid. However, in case the electrolysis be so rapid, or the current-density so large as to remove these ions

TABLE III. PRODUCTS OF ELECTROLYSIS OF AQUEOUS SOLUTIONS AT INERT ELECTRODES.

<i>Cell</i>	<i>Electrolyte</i>	<i>Cathode Products</i>	<i>Anode Products</i>
1	H ₂ SO ₄ or H ₃ PO ₄	H ₂	O ₂
2	HNO ₃ or HCl, dilute	H ₂	O ₂
3	CuSO ₄	Cu	O ₂ + H ₂ SO ₄
4	ZnSO ₄ , concentrated	Zn	O ₂ + H ₂ SO ₄
5	ZnSO ₄ + H ₂ SO ₄	H ₂	O ₂
6	Na ₂ SO ₄	H ₂ + NaOH	O ₂ + H ₂ SO ₄
7	Ba(NO ₃) ₂	H ₂ + Ba(OH) ₂	O ₂ + HNO ₃
8	NaCl, dilute	H ₂ + NaOH	O ₂ + HCl
9	NaCl, concentrated	H ₂ + NaOH	Cl ₂
10	KI or KBr	H ₂ + KOH	I ₂ or Br ₂
11	NaOH or Ba(OH) ₂	H ₂	O ₂
12	HNO ₃ , concentrated	NO ₂	O ₂
13	FeCl ₃ , concentrated	FeCl ₂	Cl ₂
14	FeCl ₂ + HCl	H ₂	FeCl ₃

from the solution near the cathode so rapidly that they are not replaced by convection or diffusion, hydrogen may be evolved.

(3) From the salts of less reducible elements, such as zinc (cell 4), cadmium, lead, or tin, the metals may be precipitated from solutions concentrated in their ions and containing little acid; but when much acid is also present (cell 5), hydrogen gas is alone evolved.

(4) From the neutral salts of the very difficultly reduced elements, such as the alkali and alkaline-earth elements, hydrogen is liberated through discharge of the hydrogen-ion, which is always present at small concentration in water, with the result that an equivalent quantity of the free base is left in the surrounding solution (cells 6–10). Even from the hydroxides of the alkali and alkaline-earth elements (cell 11) hydrogen is set free at the cathode, in spite of the extremely small concentration of hydrogen-ion in the solution.

(5) When the solution around the cathode contains an oxidizing substance (cells 12–13), like concentrated nitric acid, a ferric salt, or a chromate, this substance may be reduced and no hydrogen evolved. This is true also in case the cathode be coated with a reducible solid substance, like silver chloride, lead dioxide, or manganese dioxide.

The products at the anode include the following cases:

(1) The most common effect is the evolution of oxygen (cells 1-8). This arises from the discharge of hydroxide-ion, which is always present in the water and is more readily oxidized than most of the other anions. It results in the production of an equivalent quantity of free acid in the neighborhood of the anode.

(2) From solutions that contain chloride-ion at large concentration (cell 9), or iodide-ion or bromide-ion at any concentration (cell 10), the free halogen is liberated at the anode.

(3) In case the solution around the anode contains a reducing substance like ferrous salt (cell 14), this substance may be oxidized and no oxygen or halogen evolved.

(4) In case the anode is an oxidizable metal (unlike platinum or carbon), the change at the anode may consist only in the dissolving of the metal; thus when a nitrate or sulfate is electrolyzed with a zinc, copper, or silver anode, zinc, copper, or silver passes into solution, forming the nitrate or sulfate.

In any definite electrolytic cell, however, as already stated, the nature of the changes at the electrodes often varies with the conditions of the electrolysis, such as the temperature, applied electromotive force, current-density, rotation of the electrode, or agitation of the solution.

In the case of voltaic actions the chemical changes at the electrodes are similar, but are usually more definite since they take place under the electromotive force produced by the cell itself. They commonly consist in the solution of the metal composing the anode, and in the deposition of another metal or of hydrogen on the cathode or in the production of a soluble reduced substance at the cathode. Thus, in the Daniell cell, which consists of a copper electrode in a copper sulfate solution and of a zinc electrode in a zinc sulfate solution, the two solutions being in contact and the two electrodes connected by a metallic conductor, the zinc dissolves and the copper precipitates; and, in the Bunsen cell, which consists of a zinc electrode in dilute sulfuric acid and a carbon electrode in strong nitric acid, zinc dissolves at the anode, and the hydrogen, which is primarily produced, reduces at the cathode the nitric acid to lower oxides of nitrogen.

Prob. 6. — Chemical Changes at the Electrodes. — State what substances might be expected to be produced or destroyed at each electrode when electricity passes through: *a*, a concentrated solution of NaCl between a carbon anode and an iron cathode; *b*, a solution of NaCl between a silver anode and a silver cathode coated with AgCl; *c*, a solution of ZnSO₄ between a zinc-amalgam anode and a cathode of mercury covered with solid Hg₂SO₄; *d*, through a solution of K₂SO₄ between platinum electrodes.

10. Chemical Changes at the Electrodes: Faraday's Law.

— The most fundamental law of electrochemistry is *Faraday's law*, which may be stated as follows: The passage of electricity through an electrolyte is attended at each electrode by a chemical change involving a number of chemical equivalents N strictly proportional to the quantity of electricity Q passed through and dependent on that alone (*Faraday, 1833*). That is, denoting by F a quantity which is constant with respect to all variations of the conditions, such as temperature, concentration, current-strength, current-density,

$$Q = FN. \quad (48)$$

Such variations of conditions often influence the character of the chemical change, but not the total number of equivalents involved. The law is applicable to concentrated, as well as to dilute solutions, and to fused salts.

The constant F evidently represents the quantity of electricity producing a chemical change involving one equivalent. It is called a *faraday*, and has the value 96 494 (96 500) coulombs. One *coulomb* is the quantity of electricity flowing per second when the current is one *ampere*.

The term chemical equivalent in the above statement of Faraday's law signifies the oxidation-equivalent (*I, 9*) of the substance, for example, in the sense in which it is used in volumetric analysis. That is, *one electrochemical equivalent* of any substance is also that weight of it which is capable of oxidizing one atomic weight of hydrogen, or which has the same reducing power as one atomic weight of hydrogen.

Faraday's law gives no indication as to which of the ions that are present in the solution are involved in the chemical changes at the electrodes, nor as to the relative quantities of different ions that may be discharged or produced. All that

Faraday's law shows is that the total chemical change (the sum of the number of equivalents of all kinds of ions involved in the electrode process) is determined solely by the quantity of electricity passing through the cell.

Applications of Faraday's Law.

Prob. 7. — Through solutions of AgNO_3 , BiCl_3 , Hg_2SO_4 , and PbCl_2 , placed in series, 9650 coulombs are passed. State the number of grams of metal deposited on the cathode from each solution.

Prob. 8. — A Daniell cell, consisting of zinc in ZnSO_4 solution and copper in CuSO_4 solution, furnishes a current of 0.1 ampere for 100 minutes. How many grams of copper deposit and of zinc dissolve in the cell?

Prob. 9. — Find how long a current of 5 amperes must be passed through dilute sulfuric acid in order to produce at 27° and 1 atm., *a*, one liter of oxygen. *b*, one liter of hydrogen.
Ans. a, 52.3 min.

Prob. 10. — 1930 coulombs are passed through a solution of CuSO_4 . At the cathode 0.018 equivalent of copper is deposited. Find the number of equivalents of hydrogen that are set free.

11. The Mechanism of Conductance in Electrolytes. — Faraday's law and the laws of transference (considered below; *V*, 14) and the related phenomena have led to a development of the ionic theory which accounts for the mechanism of the conduction of electricity in electrolytes in the following way.

The passage of electricity through a metal is attended by no transfer of matter and therefore consists in the flow through the metal of free electrons (in a direction opposite to that of the current, in view of the convention long ago adopted that an electric current is a flow of positive electricity). Faraday's law shows, on the contrary, that the passage of electricity from a solution to an electrode, or in the opposite direction, is attended by the transfer to or from the electrode of an exactly corresponding quantity of some chemical substance. Or more specifically, its applications show that the passage of 96 500 coulombs of positive or negative electricity to or from an electrode is attended by the transfer to or from the electrode of exactly one oxidation-equivalent of some so-called *basic constituent* (hydrogen or a metal) of the electrolyte, or in the opposite direction of

some so-called *acidic constituent* (hydroxide, or some atom-group like nitrate, sulfate, ...). Similarly, the phenomena of transference show that through the solution itself the passage of electricity is attended by movement in opposite directions of the basic and acidic constituents of the electrolyte. These facts are sometimes briefly expressed by the statement that "motion of electricity in an electrolyte takes place only in conjunction with the motion of ions."

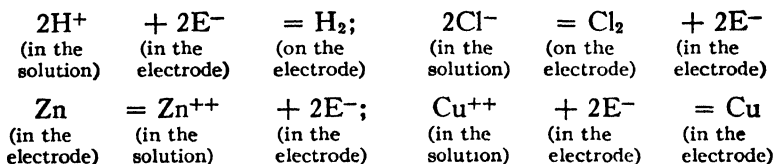
For example, in the electrolysis of concentrated hydrochloric acid, hydrogen ions move through the solution towards the cathode and there take up electrons, producing neutral hydrogen atoms and molecules; and chloride ions pass through the solution towards the anode and give off to it negative electrons, thereby producing neutral chlorine atoms and molecules. Similarly in the Daniell cell, neutral zinc atoms in the anode give up to it electrons and pass into the solution and move through it in the form of zinc ions, and copper ions move towards the cathode through the solution, and take up electrons from the cathode, thereby becoming neutral copper atoms.

Since one mol of any ion-substance has a charge of 96 500 coulombs or some simple multiple of this quantity of electricity, and since one mol consists of a definite number of molecules, namely, 6.066×10^{23} (III, 12), any ion-molecule must have a charge which is equal to or a simple multiple of a definite quantity of electricity, namely, $96\,494 / (6.066 \times 10^{23})$ or 1.591×10^{-19} coulomb. This is evidently a fundamental quantum of electricity, which, like an atom of an element, is not subdivided. This quantity of negative electricity (equal to 4.774×10^{-10} in electrostatic units) is the charge of the electron*; for the atomic structure theory (I, 5) considers that a negative ion is a neutral atom or atom-group which has combined with one or more electrons, and that a positive ion is a neutral atom or atom-group which has lost one or more electrons.

12. Expression of the Mechanism of Electrode-Reactions by Electronic Equations. — The chemical changes and the accom-

* In the experimental evaluation of these universal constants (III, 12) the above-stated relation was actually used in the converse direction; thus an exact determination of Avogadro's number has been made by measuring the charge on a single electron and dividing the value of the faraday by it.

panying electrical effects taking place at the electrodes in the way just described may be represented by *electronic equations*, in which a free electron in the electrode is represented by the symbol E^- . Thus, the electronic equations for the electrode reactions just considered are:



The electronic reaction that determines the electromotive force at an electrode often entails a further reaction that involves other substances in the solution. In such cases it may be advantageous to write a single equation expressing the net result of both reactions, thus showing all the substances actually produced and destroyed (therefore the change in state), not merely the metal and ion that may directly determine the electrode-potential. Thus in the electrolysis of a sodium chloride solution the electronic reaction determining the potential at the cathode is $2H^+ + 2E^- = H_2(g)$; but, to replace the H^+ ions thereby removed from the solution, water molecules simultaneously dissociate according to the reaction $2H_2O = 2H^+ + 2OH^-$, so that the net result of the electrode-process is expressed by the equation $2H_2O + 2E^- = H_2(g) + 2OH^-$. Another example is afforded by a lead electrode in dilute sulfuric acid: here the primary reaction when a current passes from the metal to the solution is $Pb(s) = Pb^{++} + 2E^-$; but there immediately occurs the further reaction $Pb^{++} + SO_4^{--} = PbSO_4(s)$, so that the net result is $Pb(s) + SO_4^{--} = PbSO_4(s) + 2E^-$.

In electronic equations, as in other chemical equations, the formulas of ions and electrons may represent either individual molecules and electrons, or mols of the substances and faradays of negative electricity. When it is necessary to distinguish between the individual charged molecule or ion and the substance whose molecules are charged, the terms *ion-molecule* and *ion-substance* may be used.

Prob. 11. — Formulation of Electrode-Reactions. — Formulate the primary electrode-reaction, any attendant reaction, and

the resultant reaction (showing all the substances produced and destroyed) taking place at the anode and at the cathode in each of the four electrolytic cells described in Prob. 6, which may be represented as follows:

a, C(s), NaCl(conc.) in H₂O, Fe(s).

b, Ag(s), Na⁺Cl⁻, AgCl(s) + Ag(s).

c, Pt(s), K₂⁺SO₄⁻, Pt(s).

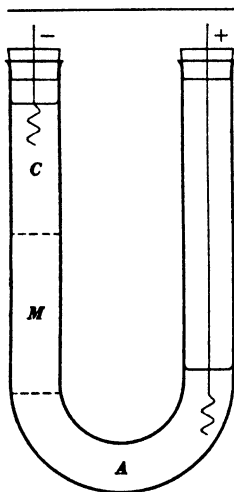
d, Zn in Hg(l), Zn⁺⁺SO₄⁻ in H₂O, Hg₂SO₄(s) + Hg(l).

Note that when a non-metallic solid substance, such as AgCl or Hg₂SO₄, is on the electrode the neighboring solution is understood to remain saturated with that substance. Note also that in chemical equations and in the formulation of voltaic cells the aggregation-state of pure substances, whether gaseous, liquid, or solid, is shown in this book by affixing the symbols (g), (l), or (s) to the chemical formulas.

III. THE TRANSFERENCE OF IONS.

13. Phenomena of Ion Transference and Its Experimental Determination.—When a current is passed through a solution of a salt, base, or acid, in addition to the chemical changes taking place at the electrodes in accordance with Faraday's law, a certain quantity of the cation-constituent is transferred from the neighborhood of the anode to that of the cathode, and a certain quantity of the anion-constituent is transferred in the reverse direction. This phenomenon (*Hittorf, 1853–1859*)

FIGURE 2.
ION TRANSFERENCE.



can best be made clear by the consideration of an actual transference determination. Consider, for example, that a 0.02 normal solution of sodium sulfate is electrolyzed at 18° in an apparatus like that shown in Fig. 2, between a platinum cathode (marked -) and a platinum anode (marked +). To avoid stirring the solution, the electrodes, from which hydrogen and oxygen gases are evolved, are placed near the surface; the anode, around which the solution becomes denser during the electrolysis, is placed near the bottom of the tube; and the apparatus is immersed in a water-bath kept at constant temperature. The current is stopped before the hydroxide-ion produced at the cathode and the hydrogen-ion produced at the anode have been transferred beyond the dotted lines in the figure. The three portions of the solution (called the cathode-portion, middle-portion, and anode-portion, and marked C, M, and A, respectively) are then separately removed from the apparatus, and submitted to analysis. The quantity of sodium and of sulfate present in each portion is compared with the quantity of it originally associated with the weight of water contained in the portion. If the experiment has been successful, the middle-portion is found to have undergone no change in composition. It is then found, per faraday of electricity passed through the solution, that the sodium-content has increased in the cathode-portion by 0.39 equivalent and has decreased in the anode-

portion by the same amount, and that the sulfate-content has increased in the anode-portion by 0.61 equivalent and has decreased in the cathode-portion by the same amount.

Prob. 12. — Resultant Effects of Transference and Electrolysis. — *a.* Write electronic equations expressing the changes produced by the electrolysis at each electrode per faraday in the experiment with sodium sulfate described above, and tabulate the number of equivalents of each ion-constituent produced per faraday by the electrolysis both in the cathode-portion and the anode-portion. *b.* Tabulate also the gain and loss caused by the transference per faraday in the number of equivalents of each ion-constituent in the cathode-portion and in the anode-portion. *c.* Tabulate the resultant effect of the electrolysis and transference on the gain and loss in the number of equivalents of sodium sulfate, sodium hydroxide, and sulfuric acid in the cathode-portion and in the anode-portion.

When either of the constituents whose transference is being determined is deposited on or dissolved off the electrode, as is the case when a lead nitrate solution is electrolyzed between lead electrodes, the quantity of it so deposited or dissolved must evidently be determined either by direct weighing or by calculation with the aid of Faraday's law, and be subtracted from or added to the observed change in content of the constituent in the electrode portion, in order to obtain the change in content produced by transference.

Prob. 13. — Determination of Transference between Reactive Electrodes. — A current is passed at 25° through a (0.1005 wn.) solution of $\text{Pb}(\text{NO}_3)_2$ containing 16.64 g. of salt in 1000 g. of water between lead electrodes until 0.1658 g. of silver is deposited in a coulometer in series with it. The anode portion weighed 62.50 g., and yielded on analysis 1.123 g. of PbCrO_4 (Noyes, Falk, 1910). *a.* Calculate the equivalents of lead transferred per faraday from the anode-portion to the cathode-portion, assuming that lead dissolved off the anode in accordance with Faraday's law. *b.* Find also the equivalents of nitrate-ion transferred in the opposite direction, assuming that lead ions and nitrate ions are the only ions present in the solution. *Ans. a,* 0.489.

The ratio of the number of equivalents N_A of any ion-constituent A transferred to the total number of faradays of electricity N which pass, whether in a solution of a single salt or a mixture of salts, is called the *transference-number* τ_A of that constituent. That is, $\tau_A = N_A/N$. Thus at 18° in a 0.02 weight-

normal solution of sodium sulfate t_{Na} is 0.39 and t_{SO_4} is 0.61, and at 25° in a 0.1005 weight-normal solution of lead nitrate t_{Pb} is 0.49 and t_{NO_3} is 0.51.

14. Hittorf's Law of Transference. — Transference determinations in aqueous solutions have shown that the sum of the number of equivalents of cation and anion transferred is equal to the number of faradays passed through the solution (*Hittorf, 1853-1859; MacInnes, Longworth, 1932*). This shows that electricity is carried through aqueous solutions only by the ions (not at all by electrons as in the case of metals). This principle may be called *Hittorf's law of transference*. This law of transference for a solution containing various positive ions A, B, ... and various negative ions E, F, ..., of which $N_A, N_B, \dots, N_E, N_F, \dots$ equivalents are transferred to the cathode and anode when N faradays of electricity pass, is obviously expressed by the equations:

$$N_A + N_B + \dots N_E + N_F + \dots = N;$$

or

$$t_A + t_B + \dots t_E + t_F + \dots = 1. \quad (49)$$

Hittorf's law obviously supplements Faraday's law, which shows that electricity is carried from solutions to electrodes, or the reverse, only by ions. There is, however, the difference that often only one kind of ion carries all the electricity to the electrodes, whereas all the ions present always take part in the conduction of it through the solution.

15. Transference in Relation to the Mobility of Ions. — The movement of the ion-constituents through the solution can be visualized by placing the solution of a salt, such as copper sulfate or potassium permanganate, whose cation or anion has a pronounced color, beneath a solution of a colorless salt, such as potassium sulfate, and applying a potential-difference between electrodes inserted in the two solutions.

The ionic theory explains the movement of the ion-constituents as resulting from a *migration of the ions* which is electrically produced in accord with the following principles. When a solution is placed between electrodes that are at different potentials, the ions in virtue of their charges are subjected to an electric force which drives them through the solution — the cations towards the cathode, the anions towards the anode.

Now the electric force f acting on any charged body is equal to its charge q multiplied by the potential-gradient; that is, $f = q (dE/dl)$, where dE is the change of potential in the distance dl . Moreover, the velocity of a body moving through a medium of great frictional resistance is proportional to the force acting upon it. Therefore, since the resistance to the motion of molecules through the solutions is very great, the absolute velocity u of any given ion is proportional to the potential-gradient; that is, $u = U (dE/dl)$, where U is the *mobility* of the ion, defined to be its velocity under unit potential-gradient.

In a case of a partially ionized substance only that part which is in the state of ions at any moment is actually moving; but the ions are continuously uniting to form unionized molecules, and the latter are continuously dissociating into ions. For this reason the resultant effect is that any ion-constituent A considered as a whole (without reference to its ionization) moves continuously towards the electrode at a linear rate v_A (under unit potential gradient) which is equal to the product of the true mobility u_{A+} or u_{A-} of the ion itself multiplied by the ionization γ of the ion-constituent; and it is only this product, that is, the mobility of the ion-constituent, which is experimentally determined by transference measurements. However, in case of a completely ionized substance, the mobilities of the ion and of the ion-constituents are of course identical, and in the case of a partially ionized substance the ratio of the mobilities of the two ion-constituents is equal to the ratio of the mobilities of the two ions.

The relation of the transference of ion-constituents to their mobilities can at once be written down when it is considered that the number N_A of equivalents of any ion-constituent A transferred in unit time under unit potential-gradient through unit cross-section of a solution is equal to the product of its mobility u_A by its volume-normal concentration c_A (per cubic centimeter). For evidently the transference-number τ_A of any ion-constituent A is correspondingly expressed by the ratio of the value of $u_A c_A$ for that ion-constituent to the sum of the values of this product for all the ion-constituents present, hence by the equation:

$$\tau_A = \frac{u_A c_A}{u_A c_A + u_B c_B + \cdots + u_N c_N + u_F c_F}. \quad (50)$$

This relation becomes in the case of a single salt with two ions A and E simply:

$$t_A = \frac{u_A}{u_A + u_E}. \quad (51)$$

That is, the ratio of the transference-numbers t_A and t_E of the two ion-constituents of any single salt A_aE is equal to the ratio of the mobilities of its two ion-constituents; that is, $t_A/t_E = u_A/u_E$.

In dealing with neutral salts, whether with single salts or with mixtures of them, in view of the conclusion previously reached (V, 6) that almost all such salts are probably nearly completely ionized up to fairly high concentrations, the expressions mobility or transference of the ions will be used in place of mobility or transference of the ion-constituents.

Prob. 14. — Transference in Relation to Ion-Mobility. — A 0.1 vn. solution of NaCl at 18° is placed in a vertical cylindrical tube 2 cm. in diameter between electrodes 20 cm. apart (consisting of perforated silver plates coated with silver chloride). At the upper electrode a potential of 50 volts is applied, and the concentration changes at the electrodes are eliminated (by steadily flowing fresh solution around them) so that the potential-gradient remains uniform throughout the tube. The mobilities of the sodium and chloride ions in this solution at 18° have been found to be 0.000373 and 0.000578 cm. per second, respectively. *a.* Sketch the apparatus approximately to scale. Calculate the distance which each of the ions moves in 30 minutes, and locate these distances in the sketch with reference to a cross-section indicated in the middle part of the tube. *b.* Calculate the number of equivalents of each ion transferred through this cross-section in 30 minutes. *c.* Calculate the transference-numbers of the two ions, and show that the ratio of them is equal to the ratio of their mobilities. *d.* Calculate the current due to the migration of each ion, and show that its transference-number is equal to the fraction of the current carried by it. *Ans. b, 0.000527 equivalent of Na.*

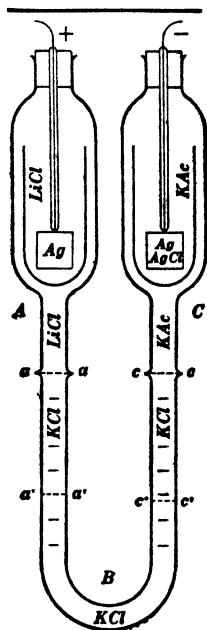
Prob. 15. — Mobility of Ions Derived from Transference Experiments. — A transference determination is made at 18° with 0.1 vn. AgNO₃ solution in a vertical tube 4 cm. in diameter between silver electrodes 30 cm. apart. Analysis of the anode-portion, which is withdrawn at the bottom, shows that 0.00207 equivalent of silver ion has migrated out of it. *a.* Sketch the apparatus, indicating a boundary of the anode-portion and a boundary of the region above it which contains all the silver ion which was transferred out of the anode portion. *b.* Calculate the distance through which the silver ion migrated

during the passage of the current, referring to the sketch for the relations involved. *c.* The potential-difference applied at the electrodes was 10 volts, and the concentration changes at the electrodes were eliminated so that the potential-gradient was uniform. The resulting current of 0.0395 ampere passed for 3 hours. Calculate the mobility in centimeters per second of each of the ions. *Ans.* *c.* 0.000520 for the NO_3^- .

16. Moving-Boundary Method of Determining Transference.—A direct method of determining the transference-number and the mobility of an ion-constituent in a definite salt solution is based on measurements of the rate of motion of a boundary between this salt solution and another salt solution, known as the indicator solution.

This method is illustrated by Fig. 3, which shows an apparatus that has been used for accurate determinations of the transference-numbers and mobilities of ions (*MacInnes, Longworth, and others, 1925–1932*). It will be described as applied to the transference of potassium-ion and of chloride-ion in potassium chloride solution. The apparatus is made in three parts: an anode vessel *A* filled with lithium chloride solution, in which is placed a silver electrode (within a cup, so that changes due to the electrolysis may not affect the rest of the solution); a cathode vessel *C* containing potassium acetate (KAc) solution and a silver electrode coated with silver chloride (also placed within a cup); and a graduated U-tube *B* with a known uniform cross-section filled with the potassium chloride solution. The three parts of the apparatus are put together (by manipulative devices not shown in the figure) so as to form a sharp boundary at the line *aa* between the lithium chloride and potassium chloride solutions, and another sharp boundary at the line *cc* between the potassium acetate and potassium chloride solutions. The boundaries are visible because of the different refractive power of the adjoining solutions. Through the apparatus placed in a

FIGURE 3.
MOVING BOUNDARY
METHOD.



thermostat a small uniform current of measured strength is passed, and the time is noted that is required for the Li-K and Ac-Cl boundaries to move through the measured distances aa' and cc' , respectively.

The ratio of the distances moved by the two boundaries is the ratio of the transference-numbers and of the mobilities of the potassium-ion and chloride-ion, provided the two arms of the apparatus have equal cross-sections so that at the same place these ions may be moving under the same potential-gradient. Furthermore, the transference-number of either of these ion-constituents can be separately calculated from the distance moved by either boundary, from the cross-section of the tube, and from the current; and the accuracy of the experimental data can be checked by determining whether the sum of these two transference-numbers is equal to unity, as Hittorf's law requires. Finally the actual mobility of each of the ions (of a completely ionized salt) can be calculated from the distance moved by either boundary and from the potential-gradient (which last can be derived by Ohm's law from the current, and electric resistance of the solution, and the cross-section of the tube).

Prob. 16. — Transference-Numbers and Ion-Mobilities Determined by the Moving-Boundary Method. — At 25° a steady current of 0.005893 ampere was passed through an apparatus like that shown in Fig. 3 containing 0.1 vn. KCl solution in the U-tube, 0.065 vn. LiCl solution in the anode compartment, and 0.070 vn. $\text{KC}_2\text{H}_3\text{O}_2$ (KAc) solution in the cathode compartment. The time required for the Li-K boundary to move through a distance of exactly 5.00 cm. was found to be 1900 seconds. The distance through which the $\text{C}_2\text{H}_3\text{O}_2$ -Cl boundary moved in the same time was 5.18 cm. The U-tube had a uniform cross-section of 0.1142 sqcm. The potential-gradient throughout the solution of potassium chloride (as calculated from its resistance and from the current) was 4.00 volts per centimeter. *a.* Calculate the ratio of the mobility and transference-number of the potassium-ion to the mobility and transference-number of the chloride-ion in the potassium chloride solution. *b.* By considering the volume swept through by the Li-K boundary, calculate the number of equivalents of potassium-ion that passed through each cross-section of the potassium chloride solution, and the corresponding transference-number of the potassium-ion. *c.* By considering the volume swept through by the other boundary, calculate the transference-number of the chloride-ion. *d.* As a test of the experimental errors, compare the transference-numbers found in

b and c with Hittorf's law of transference. e . Calculate the mobility of the potassium-ion and that of the chloride-ion in 0.1 *vn.* KCl solution at 25°. *Ans.* e , $u_K = 0.000658$ cm./sec.; $u_{Cl} = 0.000682$ cm./sec.

**** Conditions of Stability of the Moving Boundary.**

It is an essential feature of the method that the indicator ion have a smaller mobility than the ion which it follows, since otherwise the boundary does not remain sharp. In the experiment here described this requirement is met by using lithium chloride and potassium acetate as indicators, thereby causing at one boundary the less mobile lithium-ion to follow the potassium-ion, and at the other boundary the less mobile acetate-ion to follow the chloride-ion. That under these conditions the boundary tends to remain sharp is seen from the following considerations. If any quantity of lithium-ion, through migration or convection, should enter the potassium chloride solution, it would in consequence of its lesser mobility move in that solution with a smaller velocity than the potassium-ion and drop back to the boundary. The lithium-ion does not, on the other hand, as a result of its smaller mobility lag behind and thus destroy the sharpness of the boundary, because, when it begins to do so, the concentration of lithium chloride in the region behind the boundary diminishes, and this increases the resistance of the solution and therefore the potential-gradient in that region, which in turn increases the actual velocity of the ion and brings it back to the boundary.

It can be shown (Prob. 17) that the concentration of the indicator substance (Li^+Cl^-) tends to adjust itself so that the ratio of its concentration to that of the substance under investigation is equal to the ratio of the transference-number of the indicator ion (Li^+) in its solution (Li^+Cl^-) to that of the other ion (K^+) in its solution (K^+Cl^-); that is, that $c_{Li}/c_K = t_{Li}/t_K$. For these are the concentration conditions under which the two ions (Li^+ and K^+) have equal velocities in their respective solutions, and under which therefore a sharp boundary is maintained. In practice it is found necessary that the initial concentrations of the two solutions be such that their ratio conforms to this theoretical requirement within a few percent; in which case the exact adjustment of concentrations at the boundary soon automatically establishes itself.

**** Prob. 17. — Concentration Conditions in the Moving-Boundary Method.** — In a moving-boundary experiment like that described above, in order to maintain a sharp boundary, the lithium-ion in the region above the boundary aa (Fig. 3) must have the same velocity as the potassium-ion in the region below the boundary. a . Show that to fulfil this condition the ratio of the concentrations of the LiCl and KCl solutions must be equal

to the ratio of the transference-numbers of the lithium-ion and potassium-ion in the respective solutions; taking account of the fact that the current is the same throughout the whole circuit (therefore the same in the solutions of LiCl and KCl). *b.* Calculate the concentration of LiCl that should be used with 0.1 vn. KCl solution, using the mobility (0.000314 cm./sec.) of the lithium-ion in 0.1 vn. LiCl and the mobilities of the other ions found in Prob. 16 (neglecting the change in the transference-number of lithium-ion with the small change of concentration involved).

17. Values of Transference-Numbers and Their Variation with Concentration and Temperature. — In Table IV (*Longworth, 1935*) are presented all the precisely determined values of the cation-transference-numbers at 25° which have recently been obtained by the moving-boundary method. These are in fairly close agreement with the results obtained by the gravimetric method of Hittorf, so far as accurate determinations by the latter method are available.

TABLE IV. CATION-TRANSFERENCE-NUMBERS AT 25° BY THE MOVING BOUNDARY METHOD.

Salt	Equivalents per Liter				
	0.01	0.02	0.05	0.1	0.2
HCl	0.825	0.827	0.829	0.831	0.834
KCl	.490	.490	.490	.490	.489
NaCl	.392	.390	.388	.385	.382
LiCl	.329	.326	.321	.317	.311
NH ₄ Cl	.491	.491	.491	.491	.491
KBr	.483	.483	.483	.483	.484
KI	.488	.488	.488	.488	.489
KNO ₃	.508	.509	.509	.510	.512
AgNO ₃	.465	.465	.466	.468	—
NaC ₂ H ₃ O ₂	.554	.555	.557	.559	.561
CaCl ₂	.426	.422	.414	.406	.395
Na ₂ SO ₄	.385	.384	.383	.383	.383

It will be seen from Table IV that potassium, ammonium, chloride, bromide, iodide, and nitrate ions have nearly equal mobilities, and that sodium-ion has almost two thirds and lithium and acetate ions about one half this value, but that

hydrogen-ion has a much larger value, about five times that of chloride-ion.

With respect to the effect of concentration it will be noticed that the transference-number of potassium chloride does not change appreciably below 0.1 normal. It may therefore be inferred that its transference-number has this same value (0.490) as the concentration approaches zero. The values at zero concentration evidently correspond to definite ratios of the mobilities of the ions in pure water; and an accurate knowledge of even one such ratio is important, since it enables the mobilities of all the separate ions to be derived from the conductances of the salts at zero concentration by the principle of additivity (*V*, 22).

The transference-numbers of hydrochloric acid, sodium chloride, and lithium chloride change considerably with the concentration even below 0.2 normal. Thus the change in the transference-numbers in passing from 0.2 normal to 0.01 normal corresponds to a change in the ratio of the mobilities of sodium-ion and chloride-ion from 0.618 to 0.645 (or of 4.4%) and in the ratio of the mobilities of the hydrogen-ion and chloride-ion from 5.02 to 4.72 (or of 6.0%). This change in the relative mobilities of the two ions has an important bearing on the change of ion-mobility and of conductance with the concentration (*V*, 21); for it shows that a change in the absolute mobility of ions may take place even at these low concentrations. It will be seen later that the variation of the ion-mobility at these small concentrations is probably due largely to the effect of ion-attraction (*V*, 27).

As the concentration increases above 0.2 normal the transference-number often changes rapidly. This may be due to a variety of influences not much affecting the values at smaller concentrations. Thus it may arise from a change in the frictional resistance or viscosity of the medium; from hydration of the ions, which causes water to be transferred and thus affects the transference value, since this is computed under the assumption that the water is stationary; and from existence of intermediate ions or complex ions, which in concentrated solutions are more likely to be present in considerable quantity.

Increasing the temperature causes the transference-numbers of largely ionized substances to approach the value 0.5;

that is, it tends to equalize the mobilities of the two ions. For example, in 0.01 volume-normal solution the cation-transference-numbers of hydrochloric acid and of sodium chloride have the following values (*I.C.T.*, 6, 310. 1929):

	0°	18°	30°	50°
HCl	0.846	0.833	0.822	0.801
NaCl	0.387	0.397	0.404	—

18. Composition of Complex Ions Determined by Transference Experiments. — Transference measurements often show the nature of the ions present in solutions; for example the existence of complex cations or anions.

Formation of Complex Ions.

Prob. 18. — When a current is passed through a solution of potassium silver cyanide ($\text{KCN} \cdot \text{AgCN}$) silver deposits on the cathode and the cathode-portion loses 1.40 equivalents of silver and 0.80 equivalent of cyanogen, and gains 0.60 equivalent of potassium per faraday. *a.* Explain what this shows in regard to the composition of the ions and their transference-numbers. *b.* Write an electronic equation (or equations) showing the substances actually produced and destroyed.

Prob. 19. — A transference experiment is made by passing 0.01 faraday through a solution 0.2 f. in AgNO_3 and 0.6 f. in NH_3 between silver electrodes at 18°. The anode-portion is found to gain 0.0053 equivalent of silver and to lose 0.0094 formula-weight of NH_3 . Explain what this shows in regard to the composition of the ions. (Silver dissolves at the anode in accordance with Faraday's law.)

19. Hydration of Ions Investigated by Transference Measurements. — Transference experiments form the basis of one of the very few methods that furnish quantitative evidence as to the state of hydration of ions in solution. This method consists in passing a known quantity of electricity through a salt solution containing a presumably non-migrating substance like sugar, and determining in the electrode portions before and after the electrolysis not only the quantities of the ion-constituents, but also the quantity of water, associated with a definite weight of the non-migrating substance. The results are then interpreted under the assumption that the water found to be transferred to an electrode-portion, to the cathode portion for example, is equal to that brought there by the migrating cation as a result

of its hydration diminished by that carried away by the migrating anion as a result of its hydration; thus yielding information, not entirely unambiguous to be sure, as to the difference in hydration of the two ions.

It is evident, in case water is thus transferred by the ions, that the ordinary transference-numbers of the ions, often called also the *Hittorf transference-numbers*, calculated in the usual way by assuming the water to be stationary, are (at higher concentrations where the proportion of the water transferred is considerable) not accurate measures of the relative quantities of the two ions transferred. Accurate measures are, however, given by the so-called *true transference numbers*, found by determining the change in content of the ion-constituents with reference to the non-migrating substance, instead of to the water.

**** Prob. 20. — The Hydration of Ions.** — In a transference experiment (Washburn, 1908) 0.0629 faraday was passed at 25° through a solution placed between a silver anode and a silver cathode coated with silver chloride and containing 1.21 fwts. of NaCl and 0.1 fwt. of raffinose ($C_{18}H_{32}O_{16}$) in 1000 g. of water. The anode-portion was found by analysis to contain 0.96 g. less water and 1.41 g. less NaCl than was originally associated with the raffinose present in that portion. *a.* Calculate the number of mols of water and the number of equivalents of sodium transferred per faraday from the anode to the cathode, assuming that the raffinose does not migrate. *b.* Assuming no hydration of the chloride ion, calculate the number of molecules of water associated with the atom of sodium in the sodium ion. *c.* Assuming a chloride ion to be hydrated with x molecules of water, derive an expression for the hydration of the sodium ion. *d.* Calculate the Hittorf transference number of the cation, and tabulate it beside the true transference-number. *Ans. c.* $2.2 + 1.61x$ *d.* $\tau(\text{Hittorf}), 0.365$; $\tau(\text{true}), 0.383$.

Transference experiments, like that just described, have been made with various other chlorides for the purpose of determining the hydration of the ions. These experiments have led to the following mean values for the number of molecules of water per molecule of ion, assuming the mean number in a chloride ion to be x molecules (*I.C.T.*, 6, 311. 1929):

$$H^+ : 0.28 + 0.185 x.$$

$$Cs^+ : 0.67 + 1.03 x.$$

$$K^+ : 1.3 + 1.02 x.$$

$$Na^+ : 2.0 + 1.61 x.$$

$$Li^+ : 4.7 + 2.29 x.$$

IV. ELECTRICAL CONDUCTANCE OF SOLUTIONS.

20. Conductance, Specific Conductance, and Equivalent Conductance.—According to *Ohm's law*, the current i flowing between two planes of a conductor is proportional to the potential-difference E at those planes. The ratio of the current to the potential-difference is called the *conductance* L , and the inverse ratio is called the *resistance* R , of the conductor. That is,

$$i/E = L, \quad \text{and} \quad E/i = R. \quad (52)$$

When the current is expressed in amperes and the potential-difference in volts, the resistance is in ohms and the conductance in reciprocal ohms. An *ohm* is the resistance, and a *reciprocal ohm* (or *mho*) the conductance, of a column of mercury at 0° one square millimeter in cross-section and 106.3 centimeters long.

In accordance with these definitions, the conductance, expressed in reciprocal ohms, of any conductor is the number of coulombs which pass per second when the potential-difference at the ends is one volt.

The conductance of a homogeneous body of uniform cross-section is proportional to its cross-section a and inversely proportional to its length l . That is, $L = \bar{L} a/l$. The proportionality-factor $\bar{L}$, which is the conductance when the cross-section is one square centimeter and the length one centimeter, is called the *specific conductance*. Its reciprocal is called the *specific resistance* $\bar{R}$.

It has been shown by transference measurements and otherwise that in aqueous solutions of salts, acids, and bases, the ionization of the water is negligible in comparison with the concentration of the ions of the solute even when this is as small as 0.0001 normal. The conductance of such solutions therefore arises only from the motion of the ions of the salt, acid, or base; and it is convenient to employ a concept by which the conductance may be referred to one equivalent of the solute. Such a concept is *equivalent conductance* Λ , which is defined to be the conductance of that volume of solution which contains one equivalent of the salt, acid, or base, when placed between parallel electrodes one centimeter apart, at a specified temperature and pressure (assumed to be one atmosphere unless otherwise stated).

Thus the equivalent conductance $\Lambda_{0.1}$ of a salt at 0.1 volume-normal at 25° is the actual conductance at 25° of 10,000 ccm. of its 0.1 vn. solution in a cell with parallel electrodes one centimeter apart; and this actual conductance means the number of coulombs that flow per second when a potential-difference of one volt is applied at the electrodes of this cell.

Relations between Resistance, Conductance, Specific Conductance, and Equivalent Conductance.

Prob. 21. — Find the specific conductance in mhos (reciprocal ohms) of mercury at 0°.

Prob. 22. — *a.* Derive an algebraic relation expressing equivalent conductance in terms of specific conductance $\bar{\kappa}$ and of concentration $\bar{c}$ in equivalents per cubic centimeter. *b.* Calculate the specific conductances at 18° of 0.1 and 0.01 vn. NaCl solutions whose equivalent conductances at 18° are 92.0 and 101.9 reciprocal ohms, respectively.

Prob. 23. — A 0.1 normal AgNO₃ solution at 18° is placed in a tube 4 cm. in diameter between silver electrodes 12 cm. apart. A potential difference of 20 volts at the electrodes produces a current of 0.1976 ampere. Calculate the conductance, the specific conductance, and the equivalent conductance of the solution.

Prob. 24. — The equivalent conductance of a 0.01 vn. CuSO₄ solution at 18° is 71.7 reciprocal ohms. Calculate the resistance of a column of it 20 cm. long and 5 sqcm. in cross-section.

Prob. 25. — *Experimental Determination of Specific Conductance.* — In a cylindrical vessel with fixed platinum electrodes are measured in succession the resistances at 18° of a 0.01 vn. KCl solution, a 0.001 vn. K₂SO₄ solution, and the distilled water used for preparing these solutions (which has an appreciable conductance due to impurities, such as carbonic acid and ammonium hydroxide). These resistances are found to be 97.8, 937, and 100,000 ohms, respectively. *a.* Find the conductances in the vessel of the two solutions and of the water; also the conductances which the two solutions would have shown if the water had been free from the impurities (which do not react chemically with the neutral salts). *b.* From these results and the specific conductance at 18° of pure 0.01 vn. KCl solution, which is known to be 0.001225 reciprocal ohms, calculate the specific conductance of pure 0.001 vn. K₂SO₄ solution. *Ans. b.* 0.0001268.

21. Change of Equivalent Conductance with the Concentration. — The effect of the concentration on the equivalent conductance of various types of largely (probably completely)

ionized substances, often called *strong electrolytes*, is illustrated by Table V (*I.C.T.*, 6, 233-251. 1929).

TABLE V. EQUIVALENT CONDUCTANCES AT 18° OF LARGELY IONIZED SUBSTANCES AT SMALL CONCENTRATIONS.

Volume-Normality	NaCl	K ₂ SO ₄	CuSO ₄	HCl	KOH
1.0	74.19	71.5	25.74	300.5	184
0.1	91.82	94.8	43.79	350.1	213
0.02	99.40	110.1	62.32	364.9	224
0.01	101.72	115.6	71.64	369.3	228
0.005	103.54	120.1	80.87	372.4	230
0.002	105.31	124.4	91.81	375.5	233
0.001	106.27	126.7	98.42	377	234
0.0005	106.95	128.3	103.42	—	—
0.0002	107.59	129.8	—	—	—
0.0001	107.87	130.5	—	—	—
0.00	108.60	132.30	—	—	—

The equivalent conductance of all these substances is seen to increase with decreasing concentration, and at the lowest concentrations to be rapidly approaching a constant limiting value. This limiting value is called the *equivalent conductance at zero concentration* Λ_0 . By definition it is the value approached by the conductance of one equivalent of substance between parallel electrodes of indefinite extent one centimeter apart as the volume in which it is dissolved approaches infinity: it corresponds to complete ionization and to the mobilities of the ions in pure water.

At very small concentrations (below 0.001 volume-normal) the fractional decrease of the equivalent conductance Λ of largely ionized substances of all electrovalence types has been found to be proportional to the square-root of the volume-formality c of the substance. That is, denoting by β a constant for a definite substance at a definite temperature:

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \beta \sqrt{c}; \text{ or } \Lambda = \Lambda_0 (1 - \beta \sqrt{c}). \quad (53)$$

It will be shown later (*V*, 27) that this form of function is that required by the ion-attraction theory.

Moreover, the coefficient β , which is the constant ratio of the fractional decrease in the equivalent conductance of a substance to the square-root of its formality (or which is concretely the actual percentage decrease in its conductance at 0.0001 formal), has values which do not differ very greatly (namely, only by 10 to 20%) in the case of different substances of the same valence type, but which increase very markedly as the product of the electrovalences of the substance increases, namely, by from two to three fold in passing from uniunivalent to unibivalent substances, and again by about three fold in passing from unibivalent to bibivalent substances.

These statements are illustrated by the data summarized in Table VI (*Onsager, 1927; Trans. Faraday Soc.*).

TABLE VI. COEFFICIENT β OF THE FRACTIONAL DECREASE OF THE EQUIVALENT CONDUCTANCE AT 18° OF SALTS AT CONCENTRATIONS BELOW 0.001 NORMAL.

<i>Valence Type</i>	<i>Number of Salts Studied</i>	<i>Mean Value of β</i>	<i>Average Deviation of Separate Values</i>
Uniunivalent	16	0.734	0.093
Unibivalent	6	1.890	0.162
Bibivalent	2	6.30	0.34

At larger concentrations than 0.001 volume-normal the conductance decreases more slowly than proportionality to the square-root of the concentration requires (Prob. 26).

Determination of the conductance Λ_0 at zero concentration is of much importance in theoretical considerations. Its value for strong electrolytes is best obtained by applying the square-root formula (Eq. 53) to Λ values measured at concentrations between 0.001 and 0.0001 volume-normal when accurate values at these very small concentrations are available. When this is not the case a value of the coefficient β obtained at such concentrations for a closely analogous substance can be combined with a single Λ value for the substance under investigation at a somewhat higher concentration, such as 0.001 volume-normal. The Λ_0 values obtained by the square-root formula for sodium chloride and potassium sulfate (Prob. 26) are shown in Table V.

**** Prob. 26. — Derivation of Limiting Values of the Equivalent Conductance of Largely Ionized Substances.** — *a.* Plot on a large scale the equivalent conductances (Kohlrausch and others, 1900, 1904) of NaCl and K₂SO₄ given in Table V at concentrations between 0.005 and 0.0001 vn. (inclusive) against the square-root of the concentrations, and by extrapolation find values of the equivalent conductances at zero concentration. *b.* Find a numerical value of the coefficient β in Eq. 53 for each of the two salts. *c.* Calculate the equivalent conductances of NaCl and of K₂SO₄ at 0.1 vn. with the aid of these values of β ; and find the percentage deviations of the so-obtained values from those experimentally observed.

22. Equivalent Conductances of the Separate Ions. —

The specific conductance $\bar{L}$ of a solution of a salt A_a E or mixture of salts A_a E, B_b F, ... is evidently an additive property with respect to the ions present. That is, denoting by Λ_{A^+} , Λ_{B^+} , Λ_{E^-} , Λ_{F^-} , ... the equivalent conductances of the respective ions in a specific solution, and by $\bar{c}_A$, $\bar{c}_B$, $\bar{c}_E$, $\bar{c}_F$, ... the equivalent concentrations (referred to a cubic centimeter of solution) and by γ_A , γ_B , γ_E , γ_F , ... the ionization of the corresponding ion-constituents, this additivity principle is represented by the equations:

$$\bar{L} = \gamma_A \bar{c}_A \Lambda_{A^+} + \gamma_B \bar{c}_B \Lambda_{B^+} + \gamma_E \bar{c}_E \Lambda_{E^-} + \gamma_F \bar{c}_F \Lambda_{F^-}, \dots, \quad \text{for a mixture.} \quad (54)$$

$$\bar{L} = \gamma \bar{c} (\Lambda_{A^+} + \Lambda_{E^-}), \text{ for a salt } A_a E \text{ at equiv. conc. } \bar{c}. \quad (55)$$

Determination of the values of the ion-conductances and their variation with the ion-concentrations in the solution is therefore of much importance. Inasmuch as the equivalent conductance Λ of the substance divided by its ionization γ represents the sum of the conductances of its two ions, and the transference-numbers t_A and t_E represent (*V*, 15) the ratios of the mobilities or conductances of the separate ions A and E to the sum of the mobilities or conductances of the two ions, the equivalent conductances Λ_{A^+} and Λ_{E^-} of the ions of a substance A_a E at any equivalent concentration c is evidently given by the following expressions:

$$\Lambda_{A^+} = \frac{t_A \Lambda}{\gamma}; \text{ and } \Lambda_{E^-} = \frac{t_E \Lambda}{\gamma}. \quad (56)$$

Since these expressions contain the ionization γ , a quantity preliminarily unknown, they can not be immediately used

for determining the values of the ion-conductances at considerable concentrations. The *ion-conductances at zero concentration* Λ_{0A^+} , Λ_{0B^-} , where the ionization is complete ($\gamma=1$), can, however, be obtained by combining an extrapolated value Λ_0 of the equivalent conductance of a salt with extrapolated values T_{A_0} , T_{B_0} of the transference-numbers of its ion-constituents. Moreover, it suffices in principle to do this for the ions of a single salt, thus for K^+ and Cl^- in potassium chloride (a salt which is especially suitable since its transference-number changes very little with the concentration). For then the ion-conductances of the ions of other salts can be found from the Λ_0 values alone of such salts; thus Λ_{0Na^+} can be found by subtracting Λ_{0Cl^-} obtained from potassium chloride with aid of its transference-number from Λ_0 for NaCl, since this equals $\Lambda_{0Na^+} + \Lambda_{0Cl^-}$. This is in fact the method (Prob. 27) by which the values (*I.C.T.*, 6, 230, 259, 1929) of ion-conductances at zero concentration recorded in Table VII were obtained; except that the results have been checked by the use of more than one transference-number. Thus Λ_{0Cl^-} has been found to have at 25° the values 76.32, 76.32, 76.27 and 76.26 from measurements (*Longworth*, 1932) of the conductance and transference (by the moving boundary method) of potassium, sodium, lithium, and hydrogen chlorides, respectively; showing that at zero concentration a *law of independent migration of ions* applies.

Prob. 27. — Ion-Conductances at Zero Concentration Derived from Conductance and Transference Data. — Derive precise values of the ion-conductances at zero concentration at 18°, *a*, for potassium-ion and chloride-ion, and *b*, for sodium-ion and chloride-ion, from the following equivalent conductances and gravimetric transference-numbers at 18° (*I.C.T.*, 6, 233–4, 310, 1929):

Volume-Normality	Potassium Chloride		Sodium Chloride	
	Λ	T_K	Λ	T_{Na}
0.0020	—	0.496	—	0.396
0.0010	127.07	0.496	106.27	0.397
0.0005	127.86	0.496	106.95	0.397
0.0002	128.48	—	107.60	—
0.0001	128.84	—	107.88	—
0.0000	129.65	—	108.60	—

c, Derive the ion-conductance of sodium-ion also from that of potassium-ion found in *a* and from the two sets of equivalent conductance values. *Ans. b*, Na^+ , 43.1; *c*, Na^+ , 43.3.

TABLE VII. ION-CONDUCTANCES AT ZERO CONCENTRATION AT 18°.

H^+	315.2	Mg^{++}	45	OH^-	174	HCO_2^-	(47)
Li^+	33.0	Ca^{++}	51	F^-	(46.6)	$\text{C}_2\text{H}_3\text{O}_2^-$	35
Na^+	43.2	Ba^{++}	55	Cl^-	65.2	SO_4^{--}	68
K^+	64.2	Zn^{++}	(47)	Br^-	67.3	$\text{C}_2\text{O}_4^{--}$	61
Cs^+	67.5	Pb^{++}	61	I^-	66.3		
NH_4^+	64.3			NO_3^-	61.6		
Ag^+	53.8			ClO_3^-	54.9		
Ti^+	65.3			BrO_3^-	47.6		
				IO_3^-	33.8		

Examination of Table VII leads to the following generalizations regarding the ion-conductances at zero concentration:

(1) Potassium-ion and chloride-ion have nearly equal conductances (corresponding to the strikingly similar subatomic electronic structure of those ions (*I*, 5)).

(2) Neutral elementary ions of a specified subgroup of the periodic system (for example, Li^+ , Na^+ , K^+ , Cs^+ ; or Mg^{++} , Ca^{++} , Ba^{++} ; or F^- , Cl^- , Br^- , I^-) have conductances which increase at first markedly, then slowly, with increasing atomic weight. This apparent anomaly may result from decreasing hydration of such ions with increasing atomic weight (*V*, 19).

(3) The hydrogen-ion and hydroxide-ion (H^+ and OH^-) have conductances that are about 5 times and 3 times respectively as large as those of potassium-ion or chloride-ion.

(4) Compound inorganic ions (NO_3^- , ClO_3^- , BrO_3^- , IO_3^-) of similar structure decrease in conductance with increasing molecular weight.

(5) Compound ions in general, especially those of organic substances, decrease in conductance with increasing molecular weight.

Ion-conductances always increase rapidly with the temperature; thus at 18° by about 1.6% and 1.8% per degree in the case of the fast-moving hydrogen-ion and hydroxide-ion and by 2.1 to 2.6% in the case of other simple ions.

23. Conductance in Relation to the Concentration and Mobility of the Ions. — The earlier discussion of the mechanism of conduction (V, 15) shows that the specific conductance $\bar{L}$ of a solution, that is, the conductance L of a centimeter-cube between electrodes one centimeter apart, is determined for each ion by the product of the following three fundamental factors: *

(1) The number of cations $\bar{c}_A \tilde{n} \cdots$ and of anions $\bar{c}_B \tilde{n} \cdots$, that is, the number of carriers of electricity, in a centimeter-cube of solution; where $\tilde{n}$ is Avogadro's number, and $\bar{c}_A, \bar{c}_B, \cdots$ are the ion concentrations expressed as mols per cubic centimeter of solution. It may be here noted that the corresponding equivalent concentrations $\bar{c}_A, \bar{c}_B, \cdots$ of the ions are equal to $\bar{c}_A z_A, \bar{c}_B z_B, \cdots$, where $z_A, z_B, \cdots$ are the electrovalences of the ions here taken always positive.

(2) The mobilities $u_A, u_B, \cdots$ of these ions; that is, their velocities under a potential-gradient of one volt per centimeter.

(3) The quantity of electricity $z_A e, z_B e, \cdots$ carried by each ion; that is, the electric charge on each ion, equal to $z_A F/\tilde{n}, z_B F/\tilde{n}, \cdots$.

Prob. 28. — Expression for Specific Conductance Derived by Considering the Migration of Ions. — Derive the below given expression for specific conductances (Eq. 57) in terms of ion-mobilities by considering the fundamental factors named in the above text.

From these fundamental factors there is derived (Prob. 28) for the specific conductance $\bar{L}$ of any solution containing ions A, B, $\cdots$, E, F, $\cdots$ at molal concentrations $\bar{c}_A, \bar{c}_B, \cdots$ or at equivalent concentrations $\bar{c}_A, \bar{c}_B, \cdots$, and having mobilities $u_A, u_B, \cdots$, the following expression:

$$\bar{L} = \bar{c}_A u_A F + \bar{c}_B u_B F + \cdots \quad (57)$$

In the case of a single substance $A_a E$ at a formal concentration $\bar{c}$ and equivalent concentration $\bar{c}$ (equal to $a \bar{c}$) where

* Here and throughout the rest of this Chapter the plus and minus superiors showing that the property is that of the ion itself are for simplicity omitted. When the ionization is not complete the concentrations, mobilities, and conductances of the ions differ from the concentrations, mobilities, and conductances of the ion-constituents, which are the directly measured properties, by the factor $\gamma_A, \gamma_B, \cdots$ representing the fraction of the ion-constituent A, E, $\cdots$ which is in the state of free ion $A^+, E^-, \cdots$; the concentrations of the ions being less, and their mobilities and conductances being greater, in this proportion.

its ionization is γ this equation becomes:

$$\bar{L} = \gamma \bar{c} (u_A F + u_B F); \text{ or } \Lambda = \gamma (u_A F + u_B F). \quad (58)$$

Since the ionization of a substance becomes complete ($\gamma=1$) at zero concentration, its equivalent conductance Λ_0 approaches $(u_{0A} + u_{0B}) F$, and the expression for the *conductance-ratio* Λ/Λ_0 approaches:

$$\frac{\Lambda}{\Lambda_0} = \gamma \frac{u_A + u_B}{u_{0A} + u_{0B}}. \quad (59)$$

The observed decrease in the equivalent conductance of a largely ionized substance (*V*, 21) with increasing concentration may therefore be due either to decreasing ionization or to decreasing mobility of the ions or to a combination of both of these causes.

So long as the solution is so dilute that it does not differ appreciably from pure water as a viscous medium, as shown by a constant value of its viscosity η , it seemed reasonable to assume that the mobility of ions u_A , u_B in it would be the same as their mobilities u_{0A} , u_{0B} in pure water; and in the early years of the ionic theory this assumption was commonly made, and the ionization γ , even of largely ionized substances, was calculated by the first or second of the following equations:

$$\gamma = \Lambda/\Lambda_0. \quad (60)$$

$$\gamma = \Lambda \eta / \Lambda_0 \eta_0. \quad (61)$$

In the second equation η and η_0 represent the viscosities of the solution and of pure water respectively. The viscosity-ratio η/η_0 is determined by measuring the relative times required for equal volumes of the solution and of pure water to flow through the same capillary tube, when subjected to the same pressure. A film of liquid adheres firmly to the walls of the tube; and the phenomenon of the flow consists essentially in the slipping of the successive cylindrical shells of liquid past one another. Viscosity is therefore a property which depends on the frictional resistance to the motion of the molecules of the liquid past one another; and it might be expected to be roughly proportional to the frictional resistance to the motion of molecules in general through the solution.

24. Complete Ionization of Salts up to Considerable Concentrations. — It has been seen (V, 23) that the decrease in the equivalent conductance of a substance with increasing concentration may arise either from decrease in the concentration of its ions (that is, from decrease in its ionization γ) or from decrease in the mobility of its ions (diminishing from the value v_0 to some smaller value v) or from a combination of both of these causes.

In the earlier years of the ionic theory, in view of the fact that the viscosity of solutions, up to 0.1 normal for example, usually differs very little from that of pure water, so that the ions are moving apparently through a very similar medium, it was assumed that, up to concentrations of this order of magnitude, the ion-mobilities could be regarded as substantially constant and that the conductance ratio Λ/Λ_0 , or probably more exactly the conductance-viscosity ratio $\Lambda\eta/\Lambda_0\eta_0$, could be taken as a substantially exact measure of the ionization. This conclusion seemed to be confirmed by the striking fact that the ionization of salts if assumed equal to the conductance-ratio is in general nearly equal to their ionization deduced from the molar coefficient (derived from an entirely different type of properties) under the assumption that the ions and the unionized substances act as perfect solutes. Thus these two sets of values (at 18° and 0° respectively, this temperature change being shown to have very little effect on the conductance-ratio) for some typical salts at 0.1 volume-normal at 0° are shown in Table VIII (*Noyes, Falk, 1912*).

TABLE VIII. PERCENTAGE IONIZATION OF SALTS AT 0.1 VOLUME-NORMAL DETERMINED FROM CONDUCTANCE-VISCOSITY RATIOS ASSUMING CONSTANT ION-MOBILITY AND FROM MOLAR COEFFICIENTS OF THE FREEZING-POINT ASSUMING PERFECT SOLUTES.

Salt	KCl	NaNO ₃	BaCl ₂	Pb(NO ₃) ₂	Na ₂ SO ₄	MgSO ₄
$\Lambda\eta/\Lambda_0\eta_0$	86.0	83.2	75.9	63.5	70.4	44.9
γ from i	86.1	83.0	78.8	64.9	73.6	32.4

Gradually, however, there came to be recognized the improbability from a chemical standpoint of the ionization values from these assumptions (of constant ion-mobility and perfect-solute condition), and secondly the inconsistency of those values with the observed additivity up to considerable concentrations

of even those properties of solutions known to be very sensitive to molecule structure (*Noyes, 1904*). Thus the so-derived ionization values were found to be nearly equal for salts of very different chemical nature when of the same valence type, as is illustrated by the values in Table VIII. And the molar power of rotation of the plane of polarized sodium light by the sodium salt of α -bromo camphor sulfonic acid was found to have nearly equal values (272° and 270°) in 0.033 formal and in 0.0083 formal solutions, though the ionizations of the salt were 82.9 and 89.5 percent in the two cases when taken equal to the conductance-ratios (*Walden, 1894*).

Later, moreover, the development of the ion-attraction theory (*Debye-Hückel, 1923*) showed that, at any rate up to considerable concentrations such as 0.02 formal, the decrease in molar coefficient and in conductance-ratio is fully accounted for by the electrical attraction of the ions (*V, 6, 27*). The ionization of salts and of strong acids and bases is therefore now considered to be complete up to moderate concentrations; but at what point the unionized fraction becomes appreciable remains to be determined.

25. Small Concentrations of Ionized Substances Determined by Conductance Measurements. — Conductance measurements are often employed, both in scientific and technical work, for determining the concentration of the ions in solutions and deriving therefrom the concentration of the largely ionized substances that may be present.

When the ion-concentration is so small (not greater, for example, than 0.001 normal) that its influence in decreasing the mobilities of the ions can be neglected, the ion-concentration can be calculated without serious error from the measured specific conductance simply by dividing by the sum of the ion-conductances at zero concentration. When the ion-concentration is so large that its influence on the mobilities cannot be neglected, the ion-concentration is first roughly estimated with the aid of the ion-conductances at zero concentration, and the concentration of the substance is then accurately determined by dividing the specific conductance of the solution by measured values of the equivalent conductance of the substance in the neighborhood of the estimated ion-concentration.

Prob. 29. — Determination of the Solubility of Slightly Soluble Substances. — When water at 18° is saturated with silver chloride, its specific conductance is increased by 1.25×10^{-6} reciprocal ohm. Calculate the solubility of silver chloride at 18° in equivalents per liter.

Prob. 30. — Determination of the Concentrations of the Ions in Pure Water. — The specific conductance of pure water, resulting from its dissociation into H^{+} and OH^{-} , is 3.8×10^{-8} reciprocal ohm at 18° . Calculate the concentration of the ions in equivalents per liter at 18° .

Note. — The measured conductance (4.3×10^{-8} at 18°) of even the purest water that has been prepared is considerably greater than the value here given, owing to the presence of impurities; but when corrections for these impurities were made the value 3.8×10^{-8} resulted. The water ordinarily used for conductivity work, obtained by redistillation from alkaline permanganate, has a conductance 10–20 fold greater.

Prob. 31. — Determination of the Hydrolysis of Salts. — A 0.02 normal ammonium cyanide solution has at 25° a specific conductance of 0.00136 reciprocal ohm. This salt is largely hydrolyzed in accordance with the equation $NH_4CN + H_2O = NH_4OH + HCN$, and the NH_4OH and HCN are so slightly ionized in the presence of their salt as to have only a negligible conductance. The ion-conductances of NH_4^{+} and CN^{-} at zero concentration at 25° are 74.5 and 70, respectively. Assuming the equivalent conductance of unhydrolyzed ammonium cyanide decreases with the concentration in the same ratio as does that of sodium chloride (V, 21; Table V) calculate the fraction of the salt that is hydrolyzed. *Ans.* 50%.

26. Ionization of Slightly and Moderately Ionized Acids and Bases Determined by Conductance Measurements. — Although even the existence of an unionized fraction cannot be demonstrated in solutions of most salts because of the much greater effect of the ion-concentration on the ion mobility, yet conductance measurements are very useful in determining the ionization of partially ionized acids and bases. In the case of acids (or bases) that are very slightly ionized, say up to 1% at 0.1 formal, the simple equation $\gamma = \Lambda/\Lambda_0$ can be used, but with substances of greater ionization, say between 1% and 10% at 0.1 formal, a correction must be applied for the decreased ion mobility, thus as given by the expression, $\gamma = \Lambda v_0/\Lambda_0 v$. A sufficiently accurate value of v_0/v is ordinarily afforded by assuming that this mobility-ratio has the same values for the ions of the partially

ionized acid (or base) as it does for the ions of hydrochloric acid (or sodium hydroxide) at the ion-concentrations that prevail in the partially ionized solution.

Prob. 32. — Ionization of Slightly Ionized Acids and Bases Derived from Conductance Data. — *a.* Find the ionization at 18° of ammonium hydroxide at 0.1 and 0.01 n., using only the following conductance values, derived from actual conductance measurements. The Λ_0 values at 18° for NaCl, NaOH, and NH_4Cl are 108.6, 217.2, and 129.8, respectively. The equivalent conductance of ammonium hydroxide at 18° is 3.09 at 0.1 n. and 9.62 at 0.01 n. *b.* Find the ionization of H_2CO_3 into H^+ and HCO_3^- at 25° at 0.0275 vf. from the ion-conductances ($\Lambda_{\text{H}} = 350$, $\Lambda_{\text{HCO}_3} = 47$) and the fact that the specific conductance of 0.0275 vf. H_2CO_3 at 25° is 0.0000386 reciprocal ohm.

Prob. 33. — Ionization of Moderately Ionized Acids Derived from Conductance Data. — *a.* Find the sum of the conductances of the ions H^+ and H_2PO_4^- at 18° at zero concentration from data given in Table VII (V, 22) and the Λ_0 value at 18° for $\text{Na}^+\text{H}_2\text{PO}_4^-$ which is 70 (this value being corrected for the ionization of H_2PO_4^- into H^+ and HPO_4^{2-} , which is very small above 0.001 vf.). *b.* Calculate an approximate value for the ionization of the first hydrogen of H_3PO_4 at 18° and 0.05 vf., where its specific conductance is 0.006135, using for the sum of the ion-conductances the value found in *a* for zero concentration. *c.* Calculate a more exact value of its ionization by correcting for the decrease in the ion-conductances due to decreased ion-mobilities.

The ionization values for many slightly and moderately ionized acids and bases have been determined in the way just illustrated. The degree of ionization thus found at any moderate concentration as 0.1 formal varies greatly with the composition and structure of the acid or base. Such variation is shown in Table IX by the approximate values of the percentage ionization there given at 25° and 0.1 formal.

TABLE IX. PERCENTAGE IONIZATION OF ACIDS AND BASES.

H_2SO_3 (into H^+ and HSO_3^-)	35%
H_3PO_4 (into H^+ and H_2PO_4^-)	30
$\text{CH}_2\text{ClCO}_2\text{H}$	12
HNO_2 and $\text{CH}_3\text{NH}_2\text{OH}$	6
HCO_2H	4
$\text{CH}_3\text{CO}_2\text{H}$ and NH_4OH	1
H_2S , H_2CO_3 , and HClO	0.1
HCN and HBO_2	0.001

Polybasic acids are known to ionize in stages giving rise to the intermediate ion; and the first hydrogen is almost always much more dissociated than the second, and the second much more than the third. Thus H_2SO_3 at 0.1 normal and 25° is about 35% dissociated into H^+ and HSO_3^- , and less than 0.1% dissociated into H^+ and SO_3^- . Methods by which the successive hydrogens can be determined will be considered later.

27. Effect of Ion-Attraction on the Mobility of Ions. —

The ion-attraction theory leads to the conclusion that the mobility of ions decreases when their concentration increases because of two distinct effects influencing their motion. The exact mathematical treatment of these effects is complicated; but the two basic causes which give rise to them can be simply presented from a qualitative view-point.

Consider first some one negative ion surrounded by other ions. In consequence of its attraction for positive ions and its repulsion of other negative ions, there results in its immediate neighborhood an excess of positive and a deficit of negative ions (*V*, 3). This produces around the selected ion a resultant charge of positive electricity, whose density decreases with the distance from the ion (*V*, 7). When the ion is at rest, this charge is radially symmetrical around the ion; equilibrium arising from a balancing of the effect of the electric force between the ions by the effect of their kinetic molecular motion, which is constantly striving to restore their uniform distribution. But when the ion is moving in a definite direction under the influence of an electromotive force externally applied to the solution, the ion passes from a region of higher density into one of lower density of positive charge; and since the time can be shown to be not large enough to reestablish around the ion the symmetrical distribution of charge, the result is that the ion is subjected to a local electromotive force or electrostatic attraction in a direction opposite to its motion. This partially compensates the applied electromotive force and retards the motion of the ion.

A second effect arises from the fact (underlying the phenomenon of viscosity) that ions (and other molecules) moving through a solution drag along the adjacent solvent molecules. Consider again the effect on the mobility of a selected negative ion moving under an applied potential-gradient. Because of the

excess of positive ions in its neighborhood, a larger number of positive ions are moving past this ion in a counter direction than there are negative ions moving with it in the same direction. The result, since each ion drags solvent with it, is that there is a flow of solvent in the opposite direction to that in which the selected ion is moving, so that the net migration velocity of the ion is correspondingly reduced.

Both these effects are derived theoretically from the assumption that there exists around any selected ion a so-called ion-atmosphere ($V, 3$) which has a resultant positive or negative charge in consequence of the presence of excess of positive or negative ions, and from the assumption that an appreciable time is required for the production or dissipation of this ion-atmosphere. These two assumptions have received a remarkable confirmation by the experimental proof that the equivalent conductance of solutions approaches the zero concentration value when the actual conductance (given by the equation $L = I/E$) is measured by applying an extremely high electromotive force (E); for it may be assumed that each ion then moves with such high velocity that there is not time to establish the ion-atmosphere around it, and that consequently the ion moves through a neutral field such as prevails when the concentration of the salt approaches zero.

The mathematical development of this theory leads in the case of a completely ionized diionic (uniunivalent or bibivalent) substance $A E$ to the following expression for the ratio of the ion-mobilities in a solution of volume-formal concentration c to the ion-mobilities at zero concentration:

$$\frac{u_A + u_E}{u_{A_0} + u_{E_0}} = 1 - \frac{58}{\sqrt{\kappa_0} T} z \sqrt{\Sigma c z^2} \left(\frac{10^4 z}{\kappa_0 T} + \frac{1}{\eta_0 \Lambda_0} \right). \quad (62)$$

In this equation κ_0 is the dielectric constant and η_0 the viscosity of the pure solvent, z is the valence of the ions A and E , and $\Sigma c z^2$ is the double ion-strength of the solution. The first term in the parenthesis represents the correction for the attraction effect, and the second term that for the viscosity effect — the two effects described in the preceding paragraph.

Substituting sums of the conductances for the sums of the mobilities of its ions, in accordance with Eq. 59, but assuming

that the substance is completely ionized ($\gamma=1$), Eq. 62 after certain transformations becomes:

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \frac{82 z^2}{(\kappa_0 T)^{\frac{1}{2}}} \left(\frac{10^4 z}{\kappa_0 T} + \frac{1}{\Lambda_0 \eta_0} \right) \sqrt{c} \text{ (for diionic salts).} \quad (63)$$

Substituting in Eq. 63 the values κ_0 and η_0 for water at 18° , this equation assumes the simple form:

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = z^2 \left(0.225 z + \frac{50.5}{\Lambda_0} \right) \sqrt{c} \text{ (for diionic salts in H}_2\text{O at } 18^\circ\text{).} \quad (64)$$

These equations for any diionic salt A_2E and the corresponding expressions for any triionic salt A_3E show that at very small concentrations the ion-attraction causes a fractional decrease in the ion-mobilities which for any definite salt is proportional to the square-root of its concentration, and which for salts of different valence types at any definite formal concentration increases with the valence even more rapidly than the product ($z_A z_E$) of the valences of the two ions. Actual measurements have shown that these same principles apply to the fractional decrease $(\Lambda_0 - \Lambda)/\Lambda_0$ in the equivalent conductance of salts at very small concentrations (*V*, 21). These observed effects are therefore accounted for by the ion-attraction theory, provided the ionization of the salt remains complete up to the concentrations involved. But not only do the observed functional relation to concentration and the observed effect of valence accord with the general requirements of the ion-attraction theory, but the observed fractional decreases in conductance have not far from the predicted numerical values in the case of most uniunivalent salts. This evidently supports the conclusion that such substances are completely ionized, at any rate at small concentrations.

Prob. 34. — Decrease of Equivalent Conductance Predicted by the Ion-Attraction Theory in Relation to the Actual Decrease. —

a. Calculate for NaCl at 18° by Eq. 64 the theoretical value of the coefficient β in Eq. 53 (*V*, 21); and compare this theoretical value with the experimental value found in Prob. 26 (*V*, 21). *b.* Find the fractions of the theoretical value which according to the ion-attraction theory arise from the attraction effect and from the viscosity effect, respectively. *c.* Calculate by Eq. 64 the equivalent conductance of NaCl at 0.01 n. in water at 18° ,

and find the percentage divergence of this value from the observed value given in Table V (V, 21).

The degree of agreement of the observed conductances with those predicted by the ion-attraction theory under the assumption of complete ionization is illustrated by Prob. 34 and shown more fully by Table X. It will be noted that the empirical coefficient β in Eq. 53 corresponds to the coefficient of $\sqrt{c}$ in Eqs. 63 and 64. Accordingly the values of the experimental coefficient (β_{Exp}) are given in the table beside those of the theoretical coefficient (β_{Th}), and in an adjoining column are given the percentage differences, $100(\beta_{\text{Exp}} - \beta_{\text{Th}})/\beta_{\text{Th}}$, between these two quantities. The concrete significance of β will be better appreciated if it be noted that 10β represents the percentage decrease of the equivalent conductance at 0.01 formal (assuming the square-root function to hold up to that concentration).

TABLE X. EXPERIMENTAL AND THEORETICAL VALUES OF THE COEFFICIENT β OF THE DECREASE OF EQUIVALENT CONDUCTANCE Λ AT 18°.

<i>Salt</i>	β_{Exp}	β_{Th}	<i>Percent Diff.</i>	<i>Salt</i>	β_{Exp}	β_{Th}	<i>Percent Diff.</i>
LiCl	0.820	0.735	11.6	Ba(NO ₃) ₂	1.944	1.821	6.8
LiIO ₃	1.014	0.974	4.2	Sr(NO ₃) ₂	2.112	1.847	14.4
LiNO ₃	0.835	0.763	9.4	CaCl ₂	1.847	1.807	2.2
NaCl	0.710	0.688	3.2	Ca(NO ₃) ₂	2.101	1.846	13.8
NaIO ₃	0.938	0.876	7.7	MgCl ₂	1.839	1.859	- 1.1
NaNO ₃	0.782	0.705	11.0	K ₂ SO ₄	1.501	1.707	-12.1
KCl	0.652	0.614	6.3	Mean	1.890	1.815	4.1
KBr	0.666	0.607	9.6				
KI	0.558	0.612	-8.8	MgSO ₄	5.987	3.562	68.1
KIO ₃	0.779	0.739	5.4	CdSO ₄	6.616	3.546	86.6
KClO ₃	0.689	0.648	6.3	Mean	6.302	3.554	77.3
KNO ₃	0.735	0.624	17.7				
KCNS	0.632	0.642	-1.6				
CsCl	0.571	0.605	-5.5				
AgNO ₃	0.761	0.661	15.2				
TiNO ₃	0.703	0.621	13.2				
Mean	0.734	0.695	5.6				

V. ELECTROMOTIVE FORCE IN RELATION TO
CHANGES IN STATE AND IN FREE
ENERGY IN VOLTAIC CELLS.

28. Changes in State in Voltaic Cells. — Another electrical property which has been of great importance in the development of the ionic theory is the electromotive force of voltaic cells. However, before presenting this development through a consideration of cells of different types, it will be expedient to review briefly certain thermodynamic principles common to all cells, and to explain the conventions to be here adopted as regards the description of a cell, and the sign of its electromotive force.

It has already been shown (*II*, 18) that the electromotive force of any cell is fully determined by the change in state resulting from its voltaic action, as quantitatively expressed (*II*, 24) by the thermodynamic relationship $\epsilon n F = -\Delta F$. It may be recalled that in this equation ϵ is the electromotive force of the cell, and that $-\Delta F$ is the free energy decrease attending the change in state which results from the passage of n faradays of electricity through it. The numerical value of ϵ will be given a positive sign when the cell tends to produce a current of positive electricity through the cell in the direction in which it is written, and a negative sign when the cell tends to produce such a current in the opposite direction. The symbol n will denote the number of faradays of positive electricity that are considered to pass through the cell in the direction in which it is written, its numerical value being given a negative sign when positive electricity is considered to pass in the opposite direction. The free energy decrease calculated by the above equation will then have a positive sign when the cell produces electrical work, and a negative sign when external work is consumed by the cell. Its value will be in joules when the electromotive force is in volts and the quantity of electricity in coulombs.

The procedure to be pursued in deriving the electromotive-force of any cell is therefore as follows:

Formulate definitely the voltaic cell, specifying the nature of its electrodes and solutions, the concentration of each solute and the pressure of each gas, and the temperature of the cell.

Specify that a definite number of faradays n is passed through the cell from left to right; and formulate quantitatively, a , the electronic changes in state (V , 12) that occur at or near the electrodes; b , the electrical transference of ions (V , 14) that occur between the solutions of the cell; and c , the net change in state that results from the electronic reactions and the transference combined.

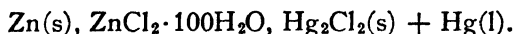
Formulate, if possible, an expression for the free energy decrease attending this change in state through a consideration of some reversible non-voltaic process to bring it about; and equate this expression with ENF .

Note that in the case of perfect solutes the free energy decrease attending the transfer of N mols of any solute from concentration c_1 to concentration c_2 is given (IV , 39) by the expression $-\Delta F = NRT \ln c_1/c_2$. Note also that this expression is only approximate when applied to ions except at small concentrations, since ions, especially those with two or more electron charges, deviate considerably (V , 7) from the condition of perfect solutes even at moderately small concentrations; but that it can be made exact (IV , 44) by substituting activities ($\alpha_1 c_1$ and $\alpha_2 c_2$) for the concentrations (c_1 and c_2), α_1 and α_2 being the correction factors or activity-coefficients.

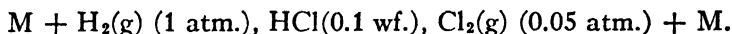
In order that there may not be a finite change in the concentrations of the solutions, and therefore in the electromotive force of the cell, during the occurrence of the change in state, it will always be considered that the solutions are present in infinite quantity, so that when a finite quantity of any substance is introduced into or withdrawn from one of the solutions of the cell there is only an infinitesimal change in its concentration. This method of consideration is much simpler for the treatment of the heat-content, free energy, and electromotive force of solutes than the closely related one, commonly employed in the formulations of the differential calculus, where the introduction of an infinitesimal quantity of the solute into a finite quantity of the solution would be considered; for it enables equivalent or molar quantities of the solute to be directly dealt with.

The character of the cell under consideration will be shown by writing the symbols of the substances and solutions in the order in which they are actually in contact with one another,

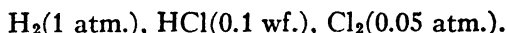
commas being inserted to indicate the junctions at which, as will be explained later, an electromotive force is produced. The conventions previously described (*I*, 12) will be employed to indicate the state of aggregation of substances and the composition of solutions. Thus a cell consisting in series of metallic zinc, of a zinc chloride solution of the composition $\text{ZnCl}_2 \cdot 100\text{H}_2\text{O}$, and of metallic mercury covered with solid mercurous chloride, at a pressure of one atmosphere (as is always understood unless some other pressure is specified), will be represented by the expression :



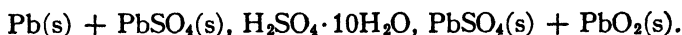
Similarly, a cell whose electrodes are an inert metal *M* in contact with hydrogen gas at 1 atm. and the same metal in contact with chlorine gas at 0.05 atm., and whose electrolyte is a 0.1 weight-formal HCl solution, will be represented by the expression :



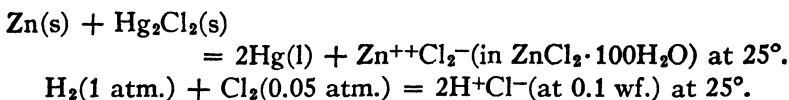
Or simply :



So also a lead storage-cell whose electrodes are lead and an inert metal coated with lead dioxide, and whose electrolyte is a sulfuric acid solution, say of the composition $\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, saturated with lead sulfate, will be represented by the expression :

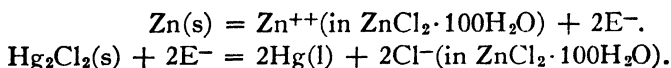


The change in state taking place in a cell may be expressed by an equation whose left-hand member represents the initial state, and whose right-hand member represents the final state, of the substances involved in the change. Thus the changes of state occurring when at 25° two faradays pass from left to right (as is always understood unless the opposite is specified) through the first two cells just formulated are shown by the equations :

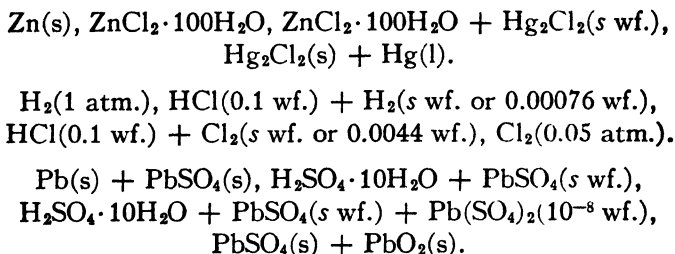


The changes in state resulting from the separate electrode processes may be expressed by electronic equations similar to

those previously described (*V*, 12), but showing also the composition of the solutions in which the ions are produced or destroyed. Thus in the case of the first of the above cells the changes in state at the anode and cathode produced by the passage of two faradays may be represented by the equations:

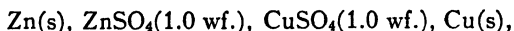


When, as in these cells, a gaseous or a solid non-metallic substance is in contact with a metal electrode, the adjoining solution is understood to be saturated with that substance. In such cells there are therefore in reality two different solutions, even though for the sake of brevity only one may be written in formulating the cell. Thus these cells ought strictly to be represented by the following expressions, in which *s* wf. denotes the weight-formal solubility of the substance in the solution in contact with it, thus of Hg_2Cl_2 in a solution of $\text{ZnCl}_2 \cdot 100\text{H}_2\text{O}$:



The recognition of the fact that there are in such cells two solutions of slightly different composition is of great importance in considering the mechanism of voltaic action and in evaluating the electrode-potentials discussed in later articles (*V*, 32, 34).

Prob. 35. — Maximum Work Attending Changes in State in Voltaic Cells. — The electromotive force at 25° of the cell,



is 1.10 volts. Give the value of *N F* in coulombs and of the electrical work in joules attending the deposition of one atomic weight of zinc on the electrode; and state what the sign of each of these quantities signifies.

Prob. 36. — Change in State in Lead Storage Cell and the Attendant Free Energy Decrease. — The electromotive force of the lead storage cell formulated above is 2.14 volts at 18°. *a.* Formulate the electronic equations which express fully the changes in state at the electrodes when $n = 2$; and derive from them the resultant change in state in the cell as a whole. (Ion transference need not be considered in this case, since the solutions at the two electrodes have substantially the same composition.) *b.* Calculate the free energy decrease in calories attending this change in state, and formulate the corresponding free energy equation. Note that the heat-content increase for this same change in state was evaluated in Prob. 64; IV, 40.

29. Electromotive Force of Cells with a Single Solution.

Determination of Ion-Activity-Coefficients. — The three cells described in the preceding article contain two solutions of substantially the same composition in the respect that in both solutions the ions present at considerable concentrations are the same, that the concentrations of these ions are substantially the same, and that the solvent medium as a whole is substantially the same. Hence, in deriving an expression for the change in state in any cell of this type, the ion-transferences need not be considered; for, though there is transference from the solution around one electrode to that around the other, this change in state is not significant, since the two solutions have substantially the same composition.

Prob. 37. — Changes in State in Cells with a Single Solution. — Formulate electronic equations which express fully the changes in state at the electrodes per faraday of electricity which passes through each of the five cells described below; and derive from these equations in each case an expression for the resultant change in state taking place in the cell as a whole.

$H_2(1 \text{ atm.}), HCl(0.1 \text{ wf.}), Cl_2(0.05 \text{ atm.});$
 $H_2(1 \text{ atm.}), KOH(0.1 \text{ wf.}), O_2(1 \text{ atm.});$
 $H_2(1 \text{ atm.}), H_2SO_4(0.01 \text{ wf.}), O_2(1 \text{ atm.});$
 $H_2(1 \text{ atm.}), HCl(0.1 \text{ wf.}), Hg_2Cl_2(s) + Hg(l);$
 $Hg(l) + HgO(s), KOH(0.5 \text{ wf.}), K_nHg(l),$

where $K_nHg(l)$ represents a solution of potassium in mercury.

The foregoing problems show that for cells of this type the resultant change in state is always a chemical one, which may involve pure liquid or solid substances (in their standard

states of unit-activity), gaseous substances at specified pressures, and solutes at specified concentrations. Two expressions for the free energy decrease may be derived,—one by considering the change in state to be brought about by the reversible action of the voltaic cell (*II*, 19, 24), and the other by a non-voltaic reversible process similar to the processes described in the derivation of the mass-action law of chemical equilibrium (*IV*, 40). By equating these two expressions, there is obtained an important relation between the electromotive force of the cell and the equilibrium constant of the cell reaction.

Prob. 38. — Calculation of Electromotive Force from Equilibrium Constants. — Calculate the electromotive force at 25° of the cell $\text{H}_2(1 \text{ atm.}), \text{H}_2\text{SO}_4(0.01 \text{ wf.}), \text{O}_2(1 \text{ atm.})$ from the equilibrium constant at 25° of the reaction $2\text{H}_2\text{O}(\text{g}) = 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$, which has been indirectly derived from equilibrium measurements at higher temperatures and found to have the value 9.7×10^{-81} . The vapor-pressure of water at 25° is 24 mm.

Note. — This method of obtaining the electromotive force is important for the following reason. The reversible electromotive force of such a cell can not be precisely determined by direct measurement because the equilibrium conditions of the electronic reaction at the oxygen electrode are not readily established.

The considerations of the preceding articles also make it possible to calculate the change that is produced in the electromotive force of a cell of this type by varying the concentration of the solutions contained in it. Thus the difference between the electromotive forces of the cells $\text{H}_2(1 \text{ atm.}), \text{HCl}(0.005 \text{ wf.}), \text{AgCl}(\text{s}) + \text{Ag}(\text{s})$ and $\text{H}_2(1 \text{ atm.}), \text{HCl}(0.5 \text{ wf.}), \text{AgCl}(\text{s}) + \text{Ag}(\text{s})$ can be derived by considering that one faraday passes through these two cells arranged in series in opposition to each other, by noting what the resultant change in state is, and by equating the two expressions for the attendant free energy decrease derived in *II*, 24 and *IV*, 39. In a combined or double cell of this type the resultant change in state will be seen to consist solely in the transfer of an ionized solute from one of the solutions present to the other.

The exact treatment of such cells is complicated by the uncertainty as to the degree of ionization of largely ionized substances and by the fact that their ions are not perfect solutes.

A rough approximation to the truth is, however, secured in electrochemical calculations, as in those relating to mass-action, by employing the hypotheses that these substances are completely ionized up to moderate concentrations, such as 1 formal, and that their ions are perfect solutes. These hypotheses are to be applied to these substances in all the problems of this chapter, unless otherwise stated. The errors to which these hypotheses lead will be indicated in some cases by a comparison of the calculated with the observed values.

Effect of Concentration on Electromotive Force.

Prob. 39. — Calculate the difference between the electromotive forces at 25° of the two cells formulated in the preceding text. Compare the result with the difference between the observed electromotive forces of these cells, which are 0.4984 and 0.2723 volt.

Prob. 40. — Calculate the difference between the electromotive force at 25° of the cell $\text{H}_2(1 \text{ atm.}), \text{HCl}(10 \text{ wf.}), \text{Cl}_2(1 \text{ atm.})$ and that of the cell $\text{H}_2(1 \text{ atm.}), \text{HCl}(6 \text{ wf.}), \text{Cl}_2(1 \text{ atm.})$. The vapor-pressures of HCl in the two solutions at 25° are 4.2 and 0.14 mm.

Prob. 41. — State what data are needed in order to calculate the electromotive force E_1 at 18° of the cell $\text{H}_2(1 \text{ atm.}), \text{H}_2\text{SO}_4(10 \text{ wf.}), \text{O}_2(1 \text{ atm.})$ from that E_2 of the cell $\text{H}_2(1 \text{ atm.}), \text{H}_2\text{SO}_4(0.01 \text{ wf.}), \text{O}_2(1 \text{ atm.})$; and formulate an expression by which the calculation could be made.

Prob. 42. — The cell $\text{Ag(s)} + \text{AgCl(s)}, \text{HCl}(0.1 \text{ wf.}), \text{Cl}_2(1 \text{ atm.})$ has at 25° an electromotive force of 1.135 volts. How much would its electromotive force be changed by substituting $\text{HCl}(0.01 \text{ wf.})$ for the $\text{HCl}(0.1 \text{ wf.})$?

Measurements with such combined or double cells form the basis of one of the important methods by which values of the mean activity-coefficients of ions can be derived. The *mean activity-coefficient* α of the ions of any specified salt, strong acid or base, is by definition equal to the geometric mean of the activity-coefficients α_A and α_B of its separate ion-constituents A and B. Thus for a diionic salt of the type $\text{A}^+ \text{B}^-$ or $\text{A}^{++} \text{B}^{--}$, $\alpha = \sqrt{\alpha_A \alpha_B}$; and for a triionic salt of the type $\text{A}_2^+ \text{B}^{--}$, $\alpha = \sqrt[3]{\alpha_A^2 \alpha_B}$.

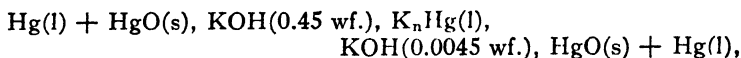
It will be evident from the following problems that the electromotive force of the double cell gives a direct measure of the free energy decrease attending the transfer of electrolyte

between the two solutions present, and that from this free energy decrease, the ratio of the products of the activities of the ions in the two solutions and of their activity-coefficients can be computed by Eq. 84, IV, 43.

*Derivation of Ion-Activity-Coefficients from
Electromotive Forces.*

Prob. 43. — *a.* From the observed values, 0.4984 and 0.2723, for the electromotive forces of the cells formulated in the text and considered in Prob. 39, calculate the ratio of the products of the activities of hydrogen-ion and chloride-ion in 0.5 weight-formal and in 0.005 weight-formal HCl solution. *b.* Calculate the corresponding ratio of the mean activity-coefficients of the ions.

Prob. 44. — At 25° 0.224 volt is the electromotive force of the cell:

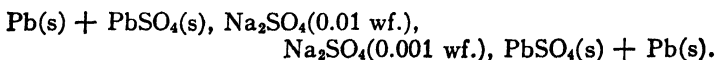
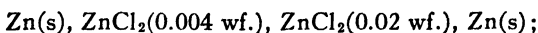
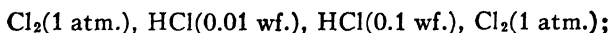
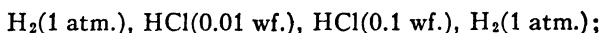


where K_nHg represents a solution of potassium in mercury of definite but unknown concentration. Calculate the ratio of the mean ion-activity-coefficients of KOH in the two solutions.

30. The Electromotive Force of Concentration Cells. —

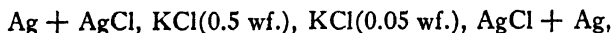
A cell which consists of two identical electrodes and two solutions containing the same substance at two different concentrations is called a *concentration cell*. The cell, $\text{Zn(s)}, \text{ZnCl}_2(0.004 \text{ wf.}), \text{ZnCl}_2(0.020 \text{ wf.}), \text{Zn(s)}$, is an example. In such cells the resultant change in state will be seen to consist solely in the transfer of an ionized solute from one of these solutions to the other.

Prob. 45. — *The Electromotive Force of Concentration-Cells.* — *a.* By proceeding in detail as described in V, 28, derive an expression for the electromotive force at T° of each of the concentration cells described below in terms of the concentrations of the two solutions, and the transference number t_c or t_a of the cation or anion of the electrolyte, assumed for such dilute solutions to be independent of the concentration. Assume complete ionization, and normal activity of the ions.



This method of finding the change in state can be much shortened by considering the direction of transfer of the ion which is *not* involved in the electronic reactions, and noting that in order to preserve electro-neutrality throughout the solution, an equivalent quantity of the other ion must be transferred, as the combined result of the electronic reactions and ion-migration, in the same direction. *b.* Calculate the electromotive force of each cell at 18°. For the first two cells use the experimentally determined transference number in 0.05 *n.* HCl, $\tau_c = 0.83$; and for the last two cells derive the transference numbers needed from the ion-conductances at zero concentration given in Table VII; *V*, 22.

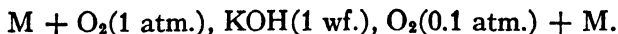
Prob. 46. — Transference Numbers from Electromotive Force Measurements. — The electromotive force at 25° of the cell,



is 0.0536 volt. The mean activity-coefficients of the ions in the 0.5 wf. and 0.05 wf. KCl solutions are 0.649 and 0.812 respectively. Calculate the transference number of the potassium ion in dilute solutions of potassium chloride (1) assuming the laws of perfect solutes, and (2) taking into consideration the deviations from such laws. Compare the results with the precise value 0.490 determined by the moving boundary method for the concentration range 0.01–0.10 normal.

Another type of concentration-cell is that in which there is a single aqueous solution in contact with electrodes consisting of some metal dissolved at two different concentrations in mercury. Since most of the metals dissolved in mercury at small concentrations have been shown by vapor-pressure and freezing-point measurements to be nearly perfect solutes having monatomic molecules, the electromotive force of cells having such solutions as electrodes can be calculated (*Prob. 61; IV, 39*) with the aid of the preceding considerations.

A similar type of concentration-cell (*Prob. 51; II, 21*) is that in which the two electrodes consist of some inert metal surrounded by the same gas at two different pressures, as in the oxygen cell,

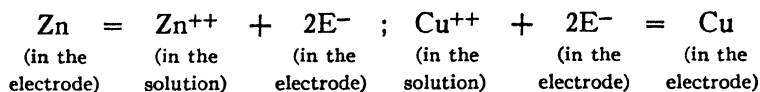


Prob. 47. — Electromotive Force of a Gas Concentration Cell. — Calculate the electromotive force at 25° of the oxygen cell formulated in the preceding text.

VI. ELECTRODE-POTENTIALS AND LIQUID-POTENTIALS.

31. Electrode-Potentials and Liquid-Potentials from Ionic View-Points. — The electromotive force produced by any voltaic cell is the algebraic sum of the electromotive forces produced at the boundaries between each electrode and the adjoining solution and at the boundaries between the different solutions. The electromotive force produced at a boundary between an electrode and a solution is called an *electrode-potential*, and that produced at a boundary between two solutions is called a *liquid-potential* (or *diffusion-potential*). In this article electrode-potentials and liquid-potentials will be interpreted qualitatively with respect to the ionic mechanism involved. In following articles they will be quantitatively considered from a thermodynamic view-point.

In any voltaic cell the electrode-potentials are the results of a tendency of an oxidation to take place at one electrode, and of a reduction to take place at the other electrode; for it is the general characteristic of an oxidation reaction that some atom involved gives up one or more of its electrons, and of a reduction reaction that some atom takes up one or more electrons from some source. Thus in the cell $\text{Zn(s)}, \text{ZnSO}_4(1 \text{ wf.}), \text{CuSO}_4(1 \text{ wf.}), \text{Cu(s)}$, zinc is oxidized to zinc-ion and copper-ion is reduced to copper at the respective electrodes in the ways expressed by the following equations:



At the specified ion-concentration (1 wf.) each of these reactions has an inherent tendency to take place. These tendencies will therefore evidently result in an accumulation of electrons, and hence of a negative charge, in the zinc electrode; and in a depletion of electrons, and hence in the production of a positive charge on the copper electrode, thus raising the copper to a higher electric potential than the zinc. In case the zinc and copper electrodes are not in metallic connection, a very slight accumulation or depletion of electrons will produce a potential-difference between each electrode and the adjoining solution sufficient to

compensate the inherent tendency of the reactions to liberate or take up electrons. When, however, the electrodes are connected by a metallic conductor, the electrons set free on the zinc flow steadily through the conductor to the copper.

Because of long-established conventions, positive (not negative) electricity is considered, and the current is said to flow through the metallic conductor from the copper to the zinc, and through the cell from the zinc to the copper, although in fact the flow of electrons is in the reverse directions; correspondingly, there is said to be a (positive) electromotive force through the cell from the zinc to the copper. And in general the total electromotive force produced by a cell is taken positive in the direction in which positive electricity tends to flow through the cell.

While the electrode-potential has been seen to be the result of the tendency of some chemical reaction of oxidation or of reduction to take place at an electrode whereby an atom of some chemical substance gives off or takes up electrons, the liquid-potential between two solutions is a purely physical phenomenon. It arises, namely, from the different rates at which the positive and the negative ions tend to diffuse, and thereby transport electricity, from one solution to the other.

Consider, for example, the boundary between two solutions of the same substance at two different concentrations, such as $\text{HCl}(1 \text{ wf.})$, $\text{HCl}(0.1 \text{ wf.})$. In this case both kinds of ions diffuse from the first to the second solution in consequence of their smaller concentrations in the latter solution; but, owing to their greater mobility, the hydrogen ions tend to pass into the second solution in larger quantity. This greater tendency of positive electricity to flow into the diluter solution is evidently equivalent to an electromotive force directed from the more concentrated to the more dilute hydrochloric acid solution.*

Consider also solutions of two different substances at the same concentration, such as $\text{HCl}(1 \text{ wf.})$, $\text{NaCl}(1 \text{ wf.})$. In this

* As a result of this tendency or this electromotive force, some excess of positive ions does in fact accumulate in the boundary when no current is flowing through the cell. A very slight quantity of ions suffices, however, to produce such a counter potential-gradient as to equalize the diffusion-rates of the two ions, by retarding the positive hydrogen ions and accelerating the negative chloride ions; and when the electric circuit is closed and a current passes through the cell, this accumulation of ions and the resulting counter-potential at once disappear.

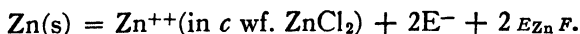
case, the hydrogen ions evidently tend to diffuse from the first solution to the second, and the sodium ions in the reverse direction; but owing to the much greater mobility of the hydrogen ions there is a resultant tendency for positive electricity to flow from the hydrochloric acid to the sodium chloride solution, this tendency constituting an electromotive force in the stated direction.

Prob. 48. — The Nature and Direction of Liquid-Potentials. — a. Explain fully, in accordance with the above statements and the values of the ion-conductances (Table VII; V, 22), the mechanism of the process by which a liquid-potential results in the case of KOH(1 wf.), KCl(1 wf.). *b.* Predict the sign of the liquid-potential of NaOH(1 wf.), NaOH(0.1 wf.); of KNO₃(1 wf.), NaCl(1 wf.); and of Na₂SO₄(0.1 wf.), Na₂SO₄(0.01 wf.). In the last case note that the molal concentration difference across the boundary for the sodium ion (0.2–0.02) is just twice that (0.1–0.01) for the sulfate ion, and assume that in consequence the diffusional forces acting on these ions differ in the same proportion.

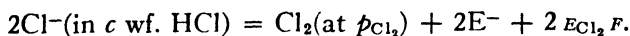
32. Electrode Potentials in Their Thermodynamic Relations. The Concept of Molal Electrode Potentials. — From the view-point of the preceding article any electronic reaction of oxidation which tends to take place at an electrode is capable of liberating electrons in the electrode, which in its electrical effect is equivalent to transferring positive electricity from the electrode to the surrounding solution. An *electrode-potential* will be here defined as the difference in potential $v_s - v_l$ between the solution and the electrode necessary to counterbalance this tendency towards oxidation. It is equal to the electromotive force $\mathcal{E}$ of the electronic reaction of oxidation; and, since a strong tendency towards oxidation is indicative of strong reducing power, it is also called its *reduction-potential*. This definition will be adhered to even for cases, exemplified by a Cu(s), CuSO₄(1 wf.) electrode, when the inherent tendency is towards an electronic reaction of reduction. In such cases the electrode-potential will be given a negative sign. Accordingly, the electromotive force of a whole cell with no liquid-potential is equal to the difference between the two opposing electrode potentials.

From a thermodynamic view-point the electrical work $\mathcal{E} N F$ producible at any definite temperature by the passage of

n faradays of positive electricity from the electrode to its surrounding solution is an exact quantitative measure of the free energy decrease $-\Delta F$ attending the corresponding electronic change in state. Thus, for the electronic change in state attending at any definite temperature the passage of two faradays at the electrode $\text{Zn(s)}, \text{ZnCl}_2(c \text{ wf.})$, the following free energy equation may be formulated:



Similarly, for the change in state corresponding to the isothermal passage of two faradays at the electrode $\text{M} + \text{Cl}_2(\text{at } p_{\text{Cl}_2} \text{ atm.}), \text{Cl}^-(\text{in } c \text{ wf. HCl})$, may be formulated the free energy equation,

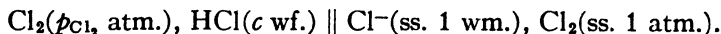


Since the molar free energy of any solute increases with its concentration, that of a gaseous substance with its pressure, and that of a pure solid substance may be considered constant,* it follows that the zinc electrode-potential E_{Zn} can be increased by decreasing the concentration of Zn^{++} , and that the chlorine electrode-potential E_{Cl_2} can be increased (made less negative) either by increasing the concentration of Cl^- or decreasing the pressure of Cl_2 .

It is evident from these two examples that an electrode-potential depends not only on the nature of the electronic reaction which produces it, but also on the states of the substances which take part in it. In the general treatment of any special case it is customary to refer the actual electrode-potential E under specified states of the substances involved in the electronic reaction to a hypothetical electrode potential E° equal to that which would be produced if each of these substances were in its standard state of unit-activity (IV, 44). Thus, pure solid or liquid substances are considered to be at 1 atm., solutes at activities 1 weight-molal, and gaseous substances at fugacities 1 atm. Such an electrode-potential is called the *molar electrode-potential* or *molar reduction-potential* of the electronic reaction of oxidation.

* In describing the change in state at the electrode the pressure of the solid and liquid phases should also be specified. It is assumed to be one atmosphere. The effect of pressure on the free energy of solids and liquids is, however, so small (II, 23) that it may be considered as negligible.

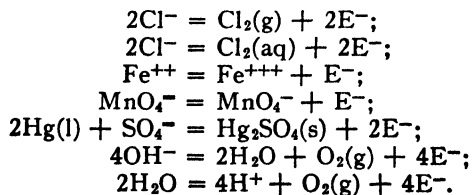
The thermodynamic relation between the actual electrode-potential E under specified states of the substances, and the molal electrode-potential E° , which is a constant characteristic of the electronic reaction, is readily obtained by deriving an expression for the electromotive force of a cell made up of the two half-cells with electrode-potentials E and E° respectively. Thus, in order to find an expression for the reduction-potential, E_{Cl_2} , of the reaction $2\text{Cl}^- = \text{Cl}_2(\text{g}) + 2\text{E}^-$ in terms of its molal reduction-potential $E^\circ_{\text{Cl}_2}$, the weight-molality of the chloride-ion (Cl^-) in the solution, and the pressure in atmospheres p_{Cl_2} , of the chlorine gas which saturates the solution at the electrode, it is only necessary to derive by the general procedure previously outlined (V, 28) an expression for the electromotive force ($E - E^\circ$) of the cell,



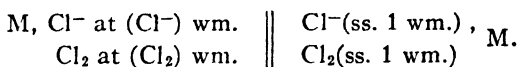
The sign $\parallel$ is here used, in place of a comma, to show that there is no liquid potential to be considered, and the formulas $\text{Cl}^-(\text{ss. 1 wm.})$ and $\text{Cl}_2(\text{ss. 1 atm.})$ to indicate that the chloride-ion and chlorine gas are in their standard states of activity, 1 weight-molal, and of fugacity 1 atm. respectively. Under the assumption of the laws of perfect solutions and gases, it will be shown in Prob. 49 that for this special case,

$$E_{\text{Cl}_2} = E^\circ_{\text{Cl}_2} - \frac{RT}{2F} \ln \frac{p_{\text{Cl}_2}}{(\text{Cl}^-)^2}.$$

Prob. 49. — Relation Between Actual and Molal Electrode-Potentials. — Derive by the method outlined above a general expression for the reduction-potential E of each of the following electronic reactions of oxidation at specified concentrations or pressures of the substances involved in terms of its molal reduction-potential E° , and of these specified concentrations or pressures. Assume the laws of perfect solutions and gases, and state how the approximate equation thereby obtained could be made exact.



Note: — If, after formulating for any special case the cell whose electromotive force is to be considered, the general relation between E , E° , and the concentrations or pressures of the substances involved in the electronic reaction can be seen by inspection, the complete derivation may be omitted. Thus, for the electronic reaction $2\text{Cl}^- = \text{Cl}_2(\text{aq}) + 2\text{e}^-$ (in which the formula $\text{Cl}_2(\text{aq})$ is used to show that the chlorine is in the dissolved state in water), the cell whose electromotive force is to be considered may be formulated as follows:



If, now, by inspection of this cell it is evident that

$$E = E^\circ - \frac{RT}{2F} \ln \frac{(\text{Cl}_2)}{(\text{Cl}^-)^2}$$

is a necessary relation, the complete proof may be omitted. Formulation of the cell and of the corresponding general relation should, however, be given for each case.

The following generalization may be made from the special cases considered in Prob. 49. The electrode potential E of any half-cell in which the change in state corresponding to the passage of n faradays from the electrode to the solution is expressed by the equation:

$$a\text{A}(\text{at } c_A) \cdots + b\text{B}(\text{at } p_B) \cdots \\ = e\text{E}(\text{at } c_E) \cdots + f\text{F} \text{ at } p_F \cdots + n\text{F}^-$$

is related to the molal electrode-potential E° of the reaction in the way shown by the expression:

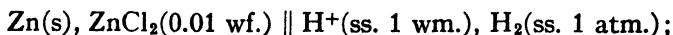
$$E = E^\circ - \frac{RT}{nF} \ln \frac{c_E^e \cdots p_F^f \cdots}{c_A^a \cdots p_B^b \cdots}. \quad (65)$$

The equation holds true strictly for perfect solutes and perfect gases, and approximately for solutes and gases at moderate concentrations or pressures. It can be made exact by substituting fugacities for the pressures of the gaseous substances, and activities for the concentrations of the solutes. In the problems of this chapter, however, unless otherwise stated, salts, strong acids and bases are to be regarded as completely ionized, and their ions are to be treated as perfect solutes up to a concentration 1 weight-molal.

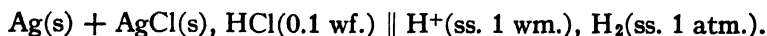
For convenience in numerical calculations it may be noted that, when common logarithms are used, the coefficient $2.303 R T/NF$ preceding the logarithmic term has the value $1.984 \times 10^{-4} T/N$ volt, or at 25° the value $0.05915/N$ volt. The last number, approximately **0.059** volt, is evidently the amount by which the electrode-potential at 25° changes when the weight-molality of any univalent ion involved in the electronic reaction is varied tenfold.

Prob. 50. — Application of Relation Between Actual and Molal Electrode-Potentials. — The potential of a platinum electrode in an acid solution of potassium iodate and iodine is found to depend only on the concentrations of H^+ , IO_3^- , and I_2 . *a.* Write the electronic reaction attending the passage of electricity from the electrode to the solution. *b.* Formulate an expression by which the electrode-potential at 25° for any small concentrations (H^+), (IO_3^-), (I_2) could be calculated from the molal electrode-potential.

33. Experimental Determination of Electrode Potentials. — Although attempts have been made to determine by various experimental methods the absolute values of electrode-potentials, yet the measurements made by these methods are not nearly so accurate nor reliable as those of the electromotive force of ordinary cells. It is therefore customary to adopt as the value of the electrode-potential of any half-cell (such as $Zn(s)$, $ZnCl_2$ (*c* wf.)) the electromotive force of a whole cell which consists of the half-cell under consideration combined with a standard half-cell. The electrode-potential of the standard half-cell is thereby assumed to be zero. Various half-cells have been used as such standards of reference; but it has now become a fairly uniform practice to employ the *molal hydrogen electrode*, $H_2(ss. 1 \text{ atm.})$, $H^+(ss. 1 \text{ wm.})$. In this book this half-cell will always be used as the standard of reference. Thus the electrode potential of the half-cell $Zn(s)$, $ZnCl_2(0.01 \text{ wf.})$ is equal to the electromotive force of the whole cell,



and the electrode potential of the half-cell $Ag(s) + AgCl(s)$, $HCl(0.1 \text{ wf.})$ is equal to the electromotive force of the cell,



It is, however, further understood that in evaluating this electromotive force the liquid-potential between the two solutions has been subtracted from the measured electromotive force of the whole cell — a fact indicated by the use of the sign $\parallel$, instead of the comma, at the liquid junction.

Table II (*V*, 9) contains some of the more accurately determined values of the molal-electrode potentials at 25°, referred to that of the molal hydrogen electrode. The following table contains a few additional values in volts.

TABLE XI. MOLAL ELECTRODE-POTENTIALS AT 25°.

<i>Reduced State</i>	<i>Oxidized State</i>	<i>Electrode Potential</i>
H ₂	2H ⁺	0.000
Cu + Cl ⁻	CuCl(s)	- 0.122
Ag + Cl ⁻	AgCl(s)	- 0.222
Hg + Cl ⁻	$\frac{1}{2}$ Hg ₂ Cl ₂ (s)	- 0.268
2OH ⁻	$\frac{1}{2}$ O ₂ + H ₂ O	- 0.398
Fe ⁺⁺	Fe ⁺⁺⁺	- 0.770
Tl ⁺	Tl ⁺⁺⁺	- 1.221
Sn ⁺⁺	Sn ⁺⁺⁺⁺	- 1.256

Evaluation of Molal Electrode-Potentials.

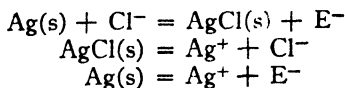
Prob. 51. — Calculate an approximate value, under the assumption of complete ionization, of the molal electrode-potential of Zn(s), Zn⁺⁺ from the fact that the cell Zn(s), ZnCl₂(0.01 wf.), HCl(0.02 wf.), H₂(g) has at 25° an electromotive force of 0.695 volt, when the hydrogen gas is slowly passed under a barometric pressure of 754 mm. through the HCl solution. The vapor-pressure of water at 25° is 24 mm., and the liquid-potential in the cell is estimated to be - 0.030 volt. *Ans.* 0.766.

Prob. 52. — The electromotive force *E* (in milli-volts) of the cell H₂(1 atm.), HCl(*c* wf.), AgCl(s) + Ag(s) has been determined at 25° at a series of concentrations *c* of hydrogen chloride (*Harned and Ehlers*, 1933) with the following results:

<i>c</i>	0.005	0.01	0.02	0.05	0.1
<i>E</i>	498.41	464.16	430.22	385.87	352.39
<i>c</i>	0.2	0.5	1.0	3.0	4.0
<i>E</i>	318.71	272.29	233.28	151.84	122.14

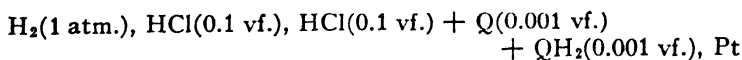
a. Calculate a value of the molal electrode-potential E° of Ag(s) + AgCl(s), Cl⁻ from the electromotive force of each of the first

five cells (1) assuming the ions to behave as perfect solutes and (2) assuming their activity-coefficients to be given by the limiting ion-attraction equation ($V, 7$), $\log \alpha = -0.505 \sqrt{\mu}$. In each case neglect the concentration (s wf.) of the dissolved AgCl in comparison with that (c wf.) of the HCl . *b.* Plot the values of E° calculated under the second assumption against the concentration c , and by extrapolation determine the limiting value at zero concentration. *c.* With the aid of the limiting value thus found calculate the mean activity-coefficient ($\alpha = \sqrt{\alpha_{\text{H}} \alpha_{\text{Cl}}}$) of the ions of HCl at each of the concentrations recorded in the table, assuming, even at the higher concentrations, complete ionization, and neglecting the concentration of dissolved AgCl . *d.* Noting that at the electrode $\text{Ag}(s) + \text{AgCl}(s)$, $\text{HCl}(c \text{ wf.})$ the equilibrium conditions of the three following reactions:



must be satisfied, that the molal reduction-potential of the first reaction was found in *b*, and that the equilibrium constant of the second reaction (or solubility-product of AgCl) is known to be 1.69×10^{-10} at 25° , calculate the molal reduction-potential of the third reaction. *Ans.* *b.* -0.2224 volt. *d.* -0.8004 volt.

Prob. 53. — At 25° the electromotive force of the cell,



is 0.699 volt, where Q represents 1,4-quinone and QH_2 its reduction-product, 1,4-hydroquinone. Formulate the electronic reaction of oxidation of hydroquinone to quinone, and find its volume-molal reduction-potential.

Note.—Quinhydrone, $\text{QH}_2 \cdot \text{Q}$, in aqueous solution produces by dissociation equimolar quantities of quinone and hydroquinone, and the potential produced at an inert electrode by its presence is accordingly determined solely by the hydrogen-ion activity in the solution. In this respect a quinhydrone electrode resembles a hydrogen electrode at a specified pressure of hydrogen.

Prob. 54. — *Electrode-Potential of the Normal Calomel Electrode.* — Calculate the electrode-potential of $\text{Hg}(l) + \text{Hg}_2\text{Cl}_2(s)$, $\text{KCl}(1 \text{ vn.})$ at 25° from the following data: The molal electrode-potential of $\text{Hg}(l) + \text{Hg}_2\text{Cl}_2(s)$, Cl^- has been computed to be -0.268 volt by the method illustrated by *Prob. 52*; a 1 vn. KCl solution is 1.033 wf. in KCl ; and the mean ion-activity coefficient of KCl in this solution is 0.600 .

The difference, -0.281 volt, between the electrode-potential of the normal calomel electrode, which is the half-cell represented by the formula $\text{Hg(l)} + \text{Hg}_2\text{Cl}_2\text{(s), KCl(1 vn.)}$, and that of the molal hydrogen electrode is a quantity of much practical importance, since other electrode-potentials are often measured directly against the normal calomel electrode, instead of against a hydrogen electrode, because of greater experimental convenience and because the liquid-potentials involved are usually much smaller.

In the investigation of the electrode-potentials of many of the electronic reactions, the electromotive measurements are not extended to solutions of sufficiently low ionic strength for the exact evaluation of the molal electrode-potential by the method described in Prob. 52. In such cases values of the molal electrode-potential are calculated from the observed values of actual electrode potentials under the assumption that the ions involved in the reaction are perfect solutes. Such values are called *formal* electrode-potentials to distinguish them from the true molal-electrode potentials. Thus for the reaction $\text{Ce}^{+++} = \text{Ce}^{++++} + \text{E}^-$, the formal electrode-potential $E^{\circ'}$ is calculated at 25° from the observed value E at the weight-formalities of the cerous and ceric ions, (Ce^{III}) and (Ce^{IV}) , by the equation,

$$E^{\circ'} = E + 0.05915 \log \frac{(\text{Ce}^{\text{IV}})}{(\text{Ce}^{\text{III}})}.$$

The corresponding expression for the true molal electrode-potential E° , involving the activity-coefficients α_{III} and α_{IV} of the cerous and ceric ion-constituents, is as follows:

$$E^\circ = E^{\circ'} + 0.05915 \log \frac{\alpha_{\text{IV}}}{\alpha_{\text{III}}}.$$

The activity-coefficients are in general unknown, but as a rule they do not show much variation over a considerable range (from about 0.2 to 1.0) of ionic strength. Accordingly the formal electrode potential may be regarded as substantially constant except in solutions of very low or very high ionic strength. For example, it has been shown (*Noyes and Garner, 1936*) that the formal cerous-ceric potential for the nitrates in nitric acid solution does not change by more than 1.5 milli-volts when the ratio

$(\text{Ce}^{\text{IV}})/(\text{Ce}^{\text{III}})$ is varied over ten-fold at constant ionic strength; and that it changes by a correspondingly small amount (-1.6085 to -1.6104 volts at 25°) when the ionic strength is varied by varying the concentration of the HNO_3 in which the salts are dissolved from 0.5 to 2.0 weight-formal. Similar relations have been found to hold true (*Kunz, 1931*) for mixtures of $\text{Ce}_2(\text{SO}_4)_3$ and $\text{Ce}(\text{SO}_4)_2$ in H_2SO_4 solutions, but the formal electrode-potentials in this case show greater variation with the ionic strength and have much smaller values, namely, -1.461 and -1.443 volts at 25° in 0.1 wf. and in 1.0 wf. H_2SO_4 respectively. This marked decrease in the formal electrode-potential may be attributed to complex formation between the ceric ion and the sulfate ion (or hydrosulfate ion).

These general conclusions are supported by the investigation of thallos-thallic, ferrous-ferric, and a number of other electrode-potentials. From a practical view-point, therefore, formal electrode-potentials are often of more value than the true molal electrode-potential, since in the calculation of actual electrode-potentials from them by Eq. 65, errors due to deviations from the laws of perfect solutes and to complex-ion formation are largely eliminated.

34. Derivation of Related Molal Electrode-Potentials from One Another. — Molal electrode-potentials that are related to one another can be calculated in the ways illustrated by the following problems.

Prob. 55. — Molal Electrode-Potentials Corresponding to Different States of Aggregation. — Calculate the molal electrode-potential at 25° *a*, of $\text{Cl}_2(1 \text{ wm.})$, Cl^- , and *b*, of $\text{I}_2(1 \text{ wm.})$, I^- , from the values given for $\text{Cl}_2(\text{g})$, Cl^- , and for $\text{I}_2(\text{s})$, I^- , in Table II (V, 9) and from the weight-molalities, 0.062 and 0.0013 of Cl_2 and I_2 in water saturated with them at 25° when the pressure is 1 atm. *Ans. a*, -1.395 ; *b*, -0.621 .

Prob. 56. — Molal Electrode-Potential of a Metal in the Presence of One of Its Slightly Soluble Salts. — Calculate the molal electrode-potential at 25° of $\text{Hg}(\text{l}) + \text{Hg}_2\text{SO}_4(\text{s})$, SO_4^{--} , from that of $\text{Hg}(\text{l})$, Hg_2^{++} given in Table II (V, 9) and from the solubility-product $[\text{Hg}_2^{++}] \times [\text{SO}_4^{--}]$ of Hg_2SO_4 which at 25° is 8.2×10^{-7} . *Ans.* -0.62 volt.

Prob. 57. — Molal Electrode-Potentials of an Element that Exists in More Than Two States of Oxidation. — *a*. Derive a rela-

tion between the molal reduction-potentials of the electronic reactions, $\text{Cu(s)} = \text{Cu}^+ + \text{E}^-$; $\text{Cu}^+ = \text{Cu}^{++} + \text{E}^-$; and $\text{Cu(s)} = \text{Cu}^{++} + 2\text{E}^-$. *b.* Calculate the second of these potentials from the other two, which are given in Table II. *c.* By a similar procedure calculate from the necessary values given in Tables II and XI the molal reduction-potentials of the reactions: $\text{Fe(s)} = \text{Fe}^{+++} + 3\text{E}^-$; $\text{Tl(s)} = \text{Tl}^{+++} + 3\text{E}^-$; and $\text{Sn(s)} = \text{Sn}^{++++} + 4\text{E}^-$. *Ans. b.* -0.22 volt.

35. The Electromotive Force of Cells with Dilute Solutions in Relation to the Molal Electrode-Potentials. — The electromotive force of cells in which the liquid-potentials are negligible or for theoretical purposes are to be disregarded can be calculated from the molal (or formal) electrode-potentials in the way illustrated by the following problems.

Evaluation of Electromotive Forces.

Prob. 58. — Calculate the electromotive force at 25° of the cell, $\text{Zn(s)}, \text{ZnCl}_2(0.001 \text{ wf.}), \text{AgCl(s)} + \text{Ag(s)}$.

Prob. 59. — Calculate the electromotive force at 25° of the cell, $\text{H}_2(0.1 \text{ atm.}), \text{HCl}(0.1 \text{ wf.}), \text{PbCl}_2(\text{s}) + \text{Pb(s)}$. The saturated solution of PbCl_2 in water at 25° is 0.039 wf.

Prob. 60. — Formulate numerical expressions for calculating the electromotive force at 25° of each of the following cells:

a. $\text{M} + \text{CuCl(s)}, \text{CuCl}_2(0.01 \text{ wf.}), \text{Cl}_2(0.1 \text{ atm.})$.

b. $\text{M}, 0.01 \text{ wf. KI sat. with } \text{I}_2 \parallel \left\{ \begin{array}{l} \text{FeCl}_2(0.02 \text{ wf.}) \\ \text{FeCl}_3(0.01 \text{ wf.}) \end{array} \right\}, \text{M}$.

The solubility-product of CuCl is 1.2×10^{-6} . In the 0.01 wf. KI solution, one half of the iodide is converted to the complex triiodide by the reaction $\text{I}^- + \text{I}_2(\text{s}) = \text{I}_3^-$.

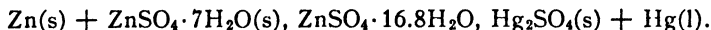
36. The Electromotive Force of Cells with Concentrated Solutions. — The electromotive force of any cell in which solutes are present at large concentrations cannot be calculated from the molal electrode-potentials with the aid of the logarithmic concentration formula (Eq. 65; V, 32) since this holds true even approximately only when the concentration does not exceed 1 formal; neither can it be calculated with the aid of the corresponding exact logarithmic activity formula, since ion-activity-coefficients at high concentrations are as a rule not independently known. A knowledge of the change in state taking place in such a cell and of the reactions occurring at its electrodes is, however,

of importance, since it shows qualitatively the factors which determine the magnitude of the electromotive force. This is illustrated by the following problems, which relate to certain cells of technical importance.

Prob. 61. — The "Dry Cell." — The Leclanche cell and the common "dry cell," which is a Leclanche cell to which some porous material, such as paper-pulp or sawdust, has been added, consists essentially of a zinc rod (amalgamated to diminish local voltaic action) dipping into a concentrated NH_4Cl solution containing ZnCl_2 , and a carbon rod coated with MnO_2 dipping into the same solution. *a.* Formulate the cell and the reaction that takes place at each electrode and the whole reaction in the cell, taking into account the facts that the MnO_2 is reduced to Mn_2O_3 , and that Zn(OH)_2 is soluble in NH_4Cl solution with formation of $\text{Zn(NH}_3)_4\text{Cl}_2$. *b.* Show in what direction the electromotive force would be changed by decreasing the concentration of the NH_4Cl .

Prob. 62. — The Edison Storage Cell. — In the nickel-iron (Edison) storage cell, $\text{Fe(s)} + \text{Fe(OH)}_2\text{(s)}$, $\text{KOH(21\%)}$, $\text{Ni(OH)}_2\text{(s)} + \text{Ni(OH)}_3\text{(s)}$, the main reaction is $\text{Fe(s)} + 2\text{Ni(OH)}_3\text{(s)} = \text{Fe(OH)}_2\text{(s)} + 2\text{Ni(OH)}_2\text{(s)}$ (the degree of hydration of the three oxides being, however, somewhat indefinite). *a.* Write the reaction occurring at each electrode. *b.* Show in what direction each of the electrode-potentials, and also the electromotive force of the whole cell, would vary with increase of the KOH concentration.

**** Prob. 63. — The Clark Standard Cell.** — One form of the Clark cell, used as a standard cell in electromotive force measurements, is at 20° represented by the formula:



a. Specify the change of state that occurs when two faradays pass through the cell. *b.* Show that even in an actual cell, with only a finite quantity of solution, no variation of the electromotive force results when two faradays pass, provided the change in state takes place slowly enough. *c.* Explain how the electromotive force of the cell would be changed by making the saturated ZnSO_4 solution also 1 formal in Na_2SO_4 .

37. Liquid-Potentials in Their Thermodynamic Relations. — There have been considered (*V*, 30) the changes in state that occur between the solutions of concentration-cells, for example at such liquid boundaries as $\text{ZnCl}_2(c_1 \text{ wf.})$, $\text{ZnCl}_2(c_2 \text{ wf.})$. In this case, assuming the transference number t_{Zn} or t_{Cl} to have the same value at the two concentrations, the transfers of ions

that take place when one faraday passes from the first to the second solution are expressed by the equations:

$$\begin{aligned}\frac{1}{2} t_{\text{Zn}} \text{Zn}^{++}(\text{in } c_1 \text{ wf. ZnCl}_2) &= \frac{1}{2} t_{\text{Zn}} \text{Zn}^{++}(\text{in } c_2 \text{ wf. ZnCl}_2). \\ t_{\text{Cl}} \text{Cl}^{-}(\text{in } c_2 \text{ wf. ZnCl}_2) &= t_{\text{Cl}} \text{Cl}^{-}(\text{in } c_1 \text{ wf. ZnCl}_2).\end{aligned}$$

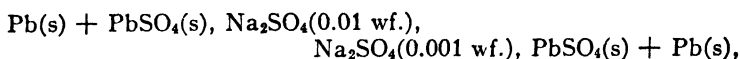
To find the liquid potential E_L , it is therefore only necessary to equate the electrical work with the free energy decrease obtainable by some other process of bringing about these same transfers of ions. Thus for the boundary just named, if the salts be considered to be completely ionized and their ions to be perfect solutes, the expression for the liquid potential evidently is:

$$E_L F = R T \left(\frac{1}{2} t_{\text{Zn}} - t_{\text{Cl}} \right) \ln \frac{c_1}{c_2}.$$

*Liquid-Potentials at the Boundaries of
Concentration-Cells.*

Prob. 64. — *a.* Calculate the liquid-potential in the cell, $\text{Zn(s)}, \text{ZnCl}_2(0.004 \text{ wf.}), \text{ZnCl}_2(0.02 \text{ wf.}), \text{Zn(s)}$, at 18° , deriving the transference-number from the ion-conductances, $\Lambda_{\text{Zn}} = 47$ and $\Lambda_{\text{Cl}} = 65.2$. *b.* Show that the values of this liquid-potential and of the electrode-potentials together make up the electromotive force of the whole cell as found in *Prob. 45*.

Prob. 65. — *a.* By considering the transfer of ions that occurs when one faraday passes through the cell,



and the corresponding free energy decrease, find an expression for the liquid-potential involved. *b.* Calculate its value at 25° , deriving the transference-number from the ion-conductances, $\Lambda_{\text{Na}} = 50.6$ and $\Lambda_{\text{SO}_4} = 78.4$.

It will be seen from the foregoing considerations that the liquid-potential between two solutions of the same salt at the two concentrations c_1 and c_2 , in the general case where the electronic charges on the cation and anion are z_c and z_a respectively, is given by the expression:

$$E_L = \left(\frac{t_c}{z_c} + \frac{t_a}{z_a} \right) \frac{R T}{F} \ln \frac{c_1}{c_2}. \quad (66)$$

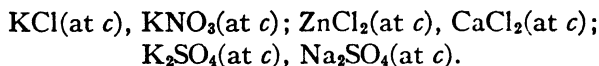
In this equation each transference-number may evidently be

replaced by the ratio of the respective ion-conductance to the sum of the two ion-conductances. The equation then becomes:

$$E_L = \frac{(\Lambda_c/z_c) + (\Lambda_a/z_a)}{\Lambda_c + \Lambda_a} \frac{R T}{F} \ln \frac{c_1}{c_2}. \quad (67)$$

These equations are exact only under the conditions that the salts are completely ionized, that the ions are perfect solutes, and that their transference numbers or relative mobilities are constant within the range of concentrations involved. In the equations the quantities z_c and z_a are to be given positive and negative values respectively corresponding to the actual charges on the cation and on the anion.

An expression can also be derived (as shown below) for the liquid-potential at the boundary between two solutions of the same concentration containing two different salts of the same valence type and with one ion in common; for example, for such combinations as,



Under the conditions that the salts are completely ionized, that the ions are perfect solutes, and that the mobility or conductance of any ion has the same value in each of the two solutions and in the mixtures of them that prevail in the boundary layers, the following equation expresses the liquid-potential directed from the first to the second solution when their equivalent conductances are Λ_1 and Λ_2 , respectively:

$$E_L = \frac{R T}{z F} \ln \frac{\Lambda_1}{\Lambda_2}. \quad (68)$$

Here z is the electronic charge on the ion not common to the two salts, its numerical value being given a positive or negative sign in correspondence with the sign of that charge.

*Evaluation of Liquid-Potentials by the
General Equations.*

Prob. 66. — Calculate the liquid-potential at 18° of the combinations: *a*, $\text{ZnSO}_4(0.010 \text{ wf.}), \text{ZnSO}_4(0.002 \text{ wf.})$; *b*, $\text{Ba(OH)}_2(0.005 \text{ wf.}), \text{Ba(OH)}_2(0.001 \text{ wf.})$. Refer to Table VII (*V*, 22) for the ion-conductances.

Prob. 67. — Calculate the liquid-potentials at 18° of the combinations: *a*, KOH(0.1 wf.), KCl(0.1 wf.); *b*, HCl(0.1 wf.), NaCl(0.1 wf.); *c*, K₂SO₄(0.01 wf.), Na₂SO₄(0.01 wf.); *d*, ZnCl₂(0.01 wf.), CaCl₂(0.01 wf.). Refer to Table VII (V, 22).

Since ions, especially bivalent and trivalent ones, deviate largely from the laws of perfect solutes even at fairly small concentrations, the expressions given above yield only roughly approximate results even at medium concentrations.

For combinations of solutions of two salts having a common ion but different concentrations, such as KNO₃(0.1 wf.), KCl(1 wf.), and for combinations of solutions of salts without a common-ion, such as KNO₃(0.1 n.), NaCl(0.01 n.), the calculation of the liquid-potential is more complicated. Combinations of these kinds can, however, be avoided by connecting the two solutions through intermediate ones so as to produce only combinations of the two types for which the liquid-potentials can be calculated by the above equations.

**** Derivation of Equation 68.**

By a consideration of the ion-transference that takes place at the boundary of the two solutions, Equation 68 can be derived with the aid of the same assumptions as those made in deriving Equation 67. Namely, taking as a specific example the combination KCl (*c* wf.), HCl(*c* wf.), it will be noted that there must be at the boundary an intermediate portion of the solution in which the two substances are present in varying proportions, the concentration of the potassium chloride decreasing continuously from left to right from *c* to 0, and that of the hydrogen chloride increasing continuously in the same direction from 0 to *c*. Considering now within the boundary-portion any two adjoining layers of infinitesimal length in which at equilibrium the prevailing concentrations of the two cation-constituents are c_K or c_H and $c_K + dc_K$ or $c_H + dc_H$ and their transference-numbers are t_K and t_H , it is evident, when one faraday passes from the KCl solution to the HCl solution, that t_K mols of potassium-ion are transferred from the concentration c_K to the concentration $c_K + dc_K$ and t_H mols of hydrogen-ion from c_H to $c_H + dc_H$. At the same time t_{Cl} equivalents of chloride-ion are transferred in the opposite direction; but this need not be considered, since its concentration is uniform throughout the whole solution. The free energy decrease $-dF$ attending this transference is therefore given by the equation:

$$-dF = -RT \left(t_K \frac{dc_K}{c_K} + t_H \frac{dc_H}{c_H} \right).$$

A corresponding transference, attended by a corresponding free energy decrease, takes place between each pair of adjoining infinitesimal layers throughout the whole boundary-portion. The total free-energy decrease, which is equal to the electrical work $E_L F$ attending the passage of one faraday, is therefore equal to the integral of this expression, taken for the c_K term between the limits $c_K = c$ and $c_K = 0$ and for the c_H term between the corresponding limits $c_H = 0$ and $c_H = c$. That is:

$$-\Delta F = E_L F = R T \int_0^c \left(T_K \frac{dc_K}{c_K} - T_H \frac{dc_H}{c_H} \right).$$

Now the transference-number of any ion-constituent is, by Equation 50 (*V*, 15), equal to the ratio of the product of its concentration by its conductance to the sum of the corresponding products for all the ion-constituents present. Hence, assuming complete or equal ionization for the two substances in all the solutions and constant ion-mobilities of the three ions up to the concentration c , the following expressions result:

$$T_K = \frac{c_K \Lambda_K}{c_K \Lambda_K + c_H \Lambda_H + c \Lambda_{Cl}}. \quad T_H = \frac{c_H \Lambda_H}{c_K \Lambda_K + c_H \Lambda_H + c \Lambda_{Cl}}.$$

Replacing c_H in the first of these expressions by $c - c_K$, and c_K in the second of these expressions by $c - c_H$, substituting the resulting values of T_K and T_H in the above free energy equation, carrying out the indicated integration, and simplifying the result by appropriate transformations, there is obtained the following equation, corresponding to Equation 68.

$$E_L F = R T \log \frac{\Lambda_K + \Lambda_{Cl}}{\Lambda_H + \Lambda_{Cl}}.$$

Prob. 68. — Derivation of the Equation for the Liquid-Potential Between Solutions with Two Solutes at the Same Concentrations. — Derive the equation just given by the method stated in the text.

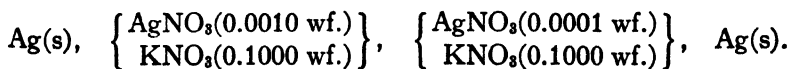
38. Ion-Concentrations Derived from Electromotive Force Measurements. — Measurements of electromotive force, interpreted with respect to the electrode-potentials involved, furnish an important means of determining ion-concentrations (strictly speaking ion-activities) which are so small that they cannot be readily measured by other methods. The so determined ion-concentrations (or ion-activities) may be used for calculating the solubilities of very slightly soluble salts, the ionization-constants of acids and bases, and other equilibrium-

constants of chemical reactions. Measurements of electromotive force similarly interpreted are frequently employed by physiologists for determining the hydrogen-ion concentration (or hydrogen-ion activity) in urine, blood, and other animal fluids, and by chemical analysts for the titration of acids and bases, especially in cases where the color of the solution makes the use of indicators unreliable.

It has been found convenient (*Sørensen, 1909*) to substitute the symbol pH for the more cumbersome $\log 1/[H^+]$ occurring in the general equation for the hydrogen electrode potential. It has in consequence become common practice to regard the pH of a solution, called the *hydrogen-ion-exponent*, as a measure of its hydrogen-ion concentration (or strictly speaking, hydrogen-ion activity). The relationship between these two quantities is perhaps more clearly brought out by writing the above definition of pH in the form, $[H^+] = 10^{-pH}$. For example, in pure water at 25° , $[H^+] = 10^{-7}$ and accordingly $pH = 7$. Each ten fold change in the hydrogen-ion concentration produces a change of only one unit in the pH of the solution, and for this reason the hydrogen-ion-exponent may be regarded as a useful foreshortened scale for measuring hydrogen-ion concentration. It should be noted that high values of pH correspond to low hydrogen-ion concentrations.

In any cell actually measured for any of these purposes, liquid-potentials are involved. Hence to derive the electrode-potentials from the measured electromotive force, the liquid-potential either must be evaluated and subtracted, or it must be made so small as to be negligible. Therefore for the practical purpose of determining ion-concentrations cells are so built up as to meet one of these conditions, as illustrated in the problems below.

The liquid-potential is negligible when the two solutions contain at the same relatively large concentration some salt whose ions are not involved in the electrode reaction. Thus the liquid-potential forms a very small fraction of the total electromotive force of the cell:



This is true inasmuch as the change in state at the boundary between the solutions consists almost wholly in the transference of K^+ and NO_3^- ions and only to a very slight extent in the transference of Ag^+ ions, and inasmuch as the transference of the former ions takes place between solutions of substantially the same concentration and is therefore attended by scarcely any change in free energy.

Prob. 69. — Solubility of Slightly Soluble Salts. — The electromotive force of the cell, $Ag(s) + AgI(s)$, $KI(0.1 \text{ wf.})$, $KNO_3(0.1 \text{ wf.})$, $AgNO_3(0.1 \text{ wf.})$, $Ag(s)$ is 0.814 volt at 25° . *a.* Evaluate the two liquid-potentials involved from the ion-conductances, which are, $\Lambda_K = 74.2$; $\Lambda_I = 76.3$; $\Lambda_{Ag} = 62.6$, and $\Lambda_{NO_3} = 70.6$. Calculate the solubility of silver iodide in 0.1 wf. KI at 25° . *c.* Making use of the solubility-product principle that in all solutions saturated with silver iodide the product $(Ag^+) \times (I^-)$ has the same value at any definite temperature, calculate the solubility of silver iodide in pure water at 25° .

Prob. 70. — Hydrogen-Ion Concentration in Aqueous Solutions. — The electromotive force of the cell,

$H_2(1 \text{ atm.})$, $HCl(0.1 \text{ wf.})$, $KCl(0.1 \text{ wf.})$, $KOH(0.1 \text{ wf.})$, $H_2(1 \text{ atm.})$

is -0.653 volt at 18° . *a.* Evaluate the liquid-potentials involved, referring to Table VII (*V*, 22) for the ion-conductances. *b.* Calculate the H^+ concentration in 0.1 wf. KOH solution at 18° . *c.* From the mass-action principle that in all dilute aqueous solutions at any definite temperature the product $(H^+) \times (OH^-)$ is a constant, called the ionization-constant of water, calculate this constant at 18° , and the concentrations of hydrogen-ion and hydroxide-ion in pure water at 18° . *d.* Suggest causes for the divergence of the result from that derived from the conductance of pure water in Prob. 30 (*V*, 25).

Prob. 71. — Dissociation of the Silver-Cyanide Complex. — The following cell has at 25° an electromotive force of 0.78 volt:

$Ag(s)$, $\left\{ \begin{array}{l} K^+Ag(CN)_2^-(0.01 \text{ wf.}) \\ KCN \quad (1 \text{ wf.}) \end{array} \right\}$, $KCl(1 \text{ wf.})$, $AgCl(s) + Ag(s)$.

The liquid-potential may be neglected since chloride-ion and cyanide-ion have nearly equal mobilities. The concentration of silver-ion (Ag^+) in a saturated solution of silver chloride in 1 wf. KCl is calculated from the solubility-product of silver chloride to be 3×10^{-10} . *a.* Calculate the concentration of silver-ion in the cyanide solution. *b.* Find the ratio of this concentration to that of the silver-cyanogen complex, and the corresponding value for the equilibrium-constant of the reaction $AgCN_2^- = Ag^+ + 2CN^-$.

Prob. 72. — Hydrogen-Ion Concentration in Solutions of Salts of Slightly Ionized Acids. — When a solution 0.05 wf. in Na_2HPO_4 is saturated with hydrogen at 1 atm., when a platinum electrode is placed in it, and when the half-cell $\text{HCl}(0.01 \text{ wf.}) + \text{NaCl}(0.1 \text{ wf.}), \text{H}_2(1 \text{ atm.})$, is brought into contact with it, the cell thus formed is found to have at 25° an electromotive force of 0.454 volt. *a.* Calculate the hydrogen-ion concentration in the Na_2HPO_4 solution, neglecting the liquid-potential, which is made small by giving to the dilute solution of hydrochloric acid a normality in sodium chloride equivalent to that of the Na_2HPO_4 . *b.* State what the result shows as to the state in which the hydrophosphate exists.

Prob. 73. — Electrometric Titration of Acids and Bases. — Into a solution of an acid to be titrated is introduced a small platinized platinum electrode, around which hydrogen gas at the barometric pressure is kept bubbling. This half-cell is placed in communication through a narrow connecting tube with a half-cell of the type $\text{NaCl}(0.1 \text{ f.}), \text{Hg}_2\text{Cl}_2(\text{s}) + \text{Hg}(\text{l})$. A standard 0.5 n. NaOH solution is added from a buret to the acid to be titrated until the electromotive force between the hydrogen electrode and the mercury electrode changes very rapidly when more alkali is added. Calculate the successive changes that would be observed in the electromotive force, when the alkali added is equivalent to 99.0, 99.5, 99.8 and 100.2% of the acid present, in case the acid to be titrated is a 0.1 normal solution of hydrochloric acid. Neglect the liquid-potential and the change in the volume of the solution produced by the addition of the standard sodium hydroxide solution.

VII. THE EQUILIBRIUM OF OXIDATION REACTIONS
IN RELATION TO THE ELECTRODE-
POTENTIALS.

39. Derivation of the Equilibrium-Constants of Oxidation Reactions from the Molal Electrode-Potentials. — When the concentrations of the substances involved in the two electrode reactions of any cell are such that the two electrode-potentials are equal to each other, there is evidently no tendency for the cell to act nor for the chemical change to take place in it. In other words, the concentrations that make the two electrode-potentials equal are concentrations at which the chemical change is in equilibrium. The equilibrium-constant of a chemical change involving solutes or gases at small concentrations or pressures can therefore be evaluated, as in the following problems, by conceiving a cell in which the reaction would take place and calculating from the molal electrode-potentials by the usual logarithmic equation the concentrations of the substances involved in the electrode reaction that will make the two actual electrode-potentials equal.

*Evaluation of Equilibrium-Constants by a
Consideration of the Equilibrium
Conditions of Voltaic Cells.*

Prob. 74. — *a.* Calculate the concentration of copper-ion at which the reaction $\text{Zn(s)} + \text{Cu}^{++} = \text{Cu(s)} + \text{Zn}^{++}$ is in equilibrium at 25° when the zinc-ion is 1 molal. *b.* Calculate the equilibrium-constant at 25° .

Prob. 75. — *a.* Calculate the concentration of hydrogen-ion at which the reaction $\text{Pb(s)} + 2\text{H}^+\text{Cl}^- = \text{H}_2(\text{g}) + \text{Pb}^{++}\text{Cl}_2^-$ is in equilibrium at 25° when the hydrogen has a pressure of 1 atm. and the lead-ion is 0.03 molal. *b.* Formulate an algebraic relation between the equilibrium-constant of the corresponding ion reaction and the molal electrode-potentials. *c.* Calculate the value of this equilibrium-constant.

The foregoing considerations evidently lead to a general expression for the equilibrium-constants of oxidation reactions. Namely, the equilibrium-constant K of the reaction which takes place when n faradays of electricity pass from left to right through a cell whose left-hand and right-hand molal electrode-

potentials are E_I° and E_g° , respectively, is related to these potentials as follows:

$$R T \log K = (E_I^\circ - E_g^\circ) N F. \quad (69)$$

This relation may be directly derived from free-energy considerations in the following way. The free energy decrease attending a chemical reaction when the reacting substances and reaction-products are all in their standard states of unit-activity (1 *wm.*) or, if gaseous, of unit fugacity (1 *atm.*) has been shown (IV, 46) to be given by the expression:

$$-\Delta F^\circ = R T \log K.$$

The free energy decrease attending this same change in state, when this is considered to take place in a cell in which all the substances are in their standard states of unit activity or fugacity, is evidently expressed by the equation:

$$-\Delta F^\circ = N F (E_I^\circ - E_g^\circ).$$

By equating these two expressions for the free energy decrease the general relation given above obviously results.

It will be evident from these considerations that any oxidation-reduction reaction reaches a state of equilibrium when the reduction-potentials of the two opposing electronic reactions of oxidation are just balanced by becoming equal, and therefore that the equilibrium constant of any oxidation-reduction reaction can be calculated from the difference between two other constants, the molal electrode-potentials of the opposing electronic reactions. Conversely, there may be calculated from the equilibrium constant of any oxidation-reduction reaction the difference between the molal reduction-potentials of its opposing electronic reactions of oxidation. Experimental investigation of the equilibrium conditions of oxidation-reduction reactions supplies accordingly an indirect method for determining molal electrode-potentials. Such methods afford not only an important check of results obtained by direct electromotive force measurement, but, as illustrated by Prob. 79, may be used to determine the reduction-potential of an electronic reaction which does not take place reversibly at an electrode, and hence does not establish in a voltaic cell its reversible electromotive force.

Evaluation of Equilibrium-Constants by the General Equation.

Prob. 76. — *a.* Derive an expression for the equilibrium-constant of the reaction $\text{Cu(s)} + \text{Cu}^{++} = 2\text{Cu}^+$ in terms of the molal reduction-potentials. *b.* Calculate the concentration of cuprous salt resulting when copper is shaken with a 0.1 wf. CuSO_4 solution at 25° . *c.* Calculate the concentration of cupric salt in the equilibrium-mixture produced by shaking a 0.1 wf. CuCl_2 solution with copper at 25° , noting that solid CuCl separates, whose solubility-product at 25° is 1.2×10^{-6} molal. *Ans.* *b*, 0.0024; *c*, 0.00172.

Prob. 77. — *a.* Calculate the equilibrium constant K_e (expressed in terms of equilibrium concentrations) of the reaction, $\text{Ag(s)} + \text{Fe}^{+++} = \text{Ag}^+ + \text{Fe}^{++}$ in a solution containing AgClO_4 , $\text{Fe(ClO}_4)_2$, and $\text{Fe(ClO}_4)_3$ (at relatively low concentrations) in 1.0 n. HClO_4 from the formal Ag(s) , Ag^+ and Fe^{++} , Fe^{+++} electrode-potentials, which in such a solution at 25° are estimated to be -0.785 and -0.728 volt, respectively. *b.* Find the composition of an equilibrium mixture obtained by shaking metallic silver with a 0.02 formal solution of $\text{Fe(ClO}_4)_3$ in 1.0 n. HClO_4 . *c.* Calculate for comparison the equilibrium constant K_a (expressed in terms of activities) from the true molal electrode-potentials recorded in Tables II (V, 9) and XI (V, 33).

Prob. 78. — Manganates in aqueous solution undergo partial decomposition into permanganates and manganese dioxide according to the following equation: $3\text{MnO}_4^- + 2\text{H}_2\text{O} = \text{MnO}_2(\text{s}) + 2\text{MnO}_4^- + 4\text{OH}^-$. Calculate the ratio of manganate to permanganate in the equilibrium mixture at 25° when in that mixture the manganate is 0.1 weight-formal and the free base is 0.01 weight-formal. The molal reduction-potentials at 25° are -0.66 volt for the reaction $\text{MnO}_4^- = \text{MnO}_4^- + \text{E}^-$ and -0.39 volt for the reaction $\text{MnO}_2(\text{s}) + 4\text{OH}^- = \text{MnO}_4^- + 2\text{H}_2\text{O} + 2\text{E}^-$. *Ans.* 12.

Prob. 79. — *Evaluation of Molal Electrode-Potentials from Equilibrium-Constants.* — The reaction $\text{Cl}_2 + \text{H}_2\text{O} + \text{H}_2\text{SeO}_3 = \text{H}_2\text{SeO}_4 + 2\text{HCl}$ is a reversible one in aqueous solution. From the equilibrium concentrations of the selenous, selenic, and hydrochloric acids in a solution saturated with chlorine gas at 1 atm. and the necessary activity-coefficients, the equilibrium-constant of the reaction $\text{Cl}_2(\text{g}) + \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} = 3\text{H}^+ + \text{HSeO}_4^- + 2\text{Cl}^-$ has been calculated to be 1.4×10^9 at 25° (*Sherrill and Izard, 1928*). Calculate the corresponding molal-reduction potential of the electronic reaction, $\text{H}_2\text{SeO}_3 + \text{H}_2\text{O} = 3\text{H}^+ + \text{HSeO}_4^- + 2\text{E}^-$. *b.* Calculate the equilibrium constant of the reaction $\text{Br}_2 + \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} = 3\text{H}^+ + \text{HSeO}_4^- + 2\text{Br}^-$. Refer to Table II (V, 9) for the additional data needed.

VIII. VOLTAIC ACTION ELECTROLYSIS AND POLARIZATION.

40. Concentration-Changes Attending Voltaic Action and the Resulting Polarization. — Throughout the foregoing considerations, as an aid in evaluating the electromotive force, it has been assumed that so large a quantity of solution is present in the cell that only infinitesimal concentration-changes are produced in it by the passage of a finite quantity of electricity. The fact that this is not the case in actual cells must be taken into account, as in the following problem.

Prob. 80. — Change of Electromotive Force due to Changes in Concentration. — The electromotive force E at 15° of the lead storage-cell varies with the mol-fraction X of the H_2SO_4 (for values of X up to 0.10) according to the equation $E = 1.855 + 3.80 X - 10 X^2$. Out of a certain cell which contains 1300 g. of 10 mol-percent H_2SO_4 a steady current of 5.36 amperes is taken for 10 hours. Calculate the electromotive force of the cell at the beginning and at the end.

In practice the electromotive force is often decreased much more than these considerations indicate because the concentration-changes actually occur in the immediate neighborhood of the electrodes and are only gradually distributed by convection or diffusion through the whole body of the solution. Thus in the lead storage-cell water is produced and acid is destroyed by the electrode reaction in the solution impregnating the porous lead-peroxide electrode, and the acid can only be replenished from the main body of the solution by the slow process of diffusion. This phenomenon is one kind of polarization, sometimes called *concentration-polarization*; the name *polarization* being used in general to denote the production by the passage of the current of any change in the solution adjoining the electrode or in the surface of the electrode which makes its potential deviate from its normal value.

Concentration-polarization is affected by various incidental conditions, for example, by agitation of the solution around the electrodes. It is also often greatly influenced by the *current-density*, by which is meant the current per unit-area of electrode surface, thus the number of amperes per square centimeter or square decimeter of surface of a specified electrode.

Prob. 81. — Concentration-Polarization and the Factors Affecting It. — When a current is taken at 25° out of a certain cell of the form $\text{Zn(s)}, \text{ZnSO}_4(1 \text{ wf.}), \text{CuSO}_4(1 \text{ wf.}), \text{Cu(s)}$, the electromotive force soon becomes fairly constant and remains so for a time at a value 0.06 volt below its normal value. *a.* Show quantitatively how this might be accounted for by concentration-polarization. *b.* Explain how the polarization would be affected by increasing the current; by using smaller electrodes without changing the current, thereby increasing the current-density; and by stirring the solutions, these being separated from each other by a porous cup.

41. Electrolysis in Relation to Minimum Decomposition-Potential. — In order to produce electrolysis in any electrolytic cell there must obviously be applied from an external source an electromotive force at least equal to the electromotive force that is produced by the combination of solution and electrodes, considering it as a voltaic cell. The value of the electromotive force that must be applied to compensate the electromotive force of the voltaic cell which develops under the actual conditions, assuming local concentration changes to be equalized, may be called the *minimum decomposition-potential*. Its value can evidently be calculated in the case of cells with dilute solutions by the method considered in V, 35. It is important to recognize this fact; for the decomposition-potential is sometimes treated as if it were an essentially independent quantity. The *actual decomposition-potential*, that is, the electromotive force that must be applied to produce continuous electrolysis, may be much greater than the minimum decomposition-potential because of polarization effects, such as are considered in the next article.

Prob. 82. — Deposition of Metals by Electrolysis. — A solution 0.05 wf. in H_2SO_4 and 0.05 wf. in CuSO_4 is electrolyzed at 25° between a mercury anode and a platinum cathode. In the mixture assume the salt to be completely ionized and the acid to be 35% ionized into 2H^+ and SO_4^- and 65% ionized into H^+ and HSO_4^- . *a.* Calculate from the molal electrode-potentials (taking that of $\text{Hg(l)} + \text{Hg}_2\text{SO}_4(\text{s}), \text{SO}_4^-$ to be -0.62 volt) the minimum electromotive force which would have to be applied in order to cause the copper to deposit. *b.* Find the value to which this electromotive force would have to be increased after 99% of the copper had been precipitated in order that the deposition might continue, assuming the ionizations to be the same as in the original

mixture. *c.* Find the minimum electromotive force at which hydrogen could be continuously set free, assuming that it attains at the cathode an effective pressure of 1 atm.

Prob. 83. — Separation of Elements by Electrolysis. — A solution 0.1 wf. in KCl, 0.1 wf. in KBr, and 0.1 wf. in KI is placed, together with a platinum electrode, in a porous cup; and this is placed within a larger vessel containing a zinc electrode and a large quantity of 0.1 wf. ZnCl_2 solution. Neglecting the liquid-potential and any polarization effects, calculate the applied electromotive force required at 25° , *a*, to liberate 99.9% of the iodine; *b*, to set bromine free at a concentration of 0.0001 wm.; *c*, to liberate 99.9% of the bromine (which remains in solution); and *d*, to liberate chlorine at a concentration of 0.0001 weight-molal.

42. Electrolysis in Relation to Polarization. — In electrolysis, as in voltaic action, concentration changes are produced in the solutions around the electrodes; and these changes have the effect of increasing the applied electromotive force required. Thus in electrolyzing a copper solution between copper electrodes (as is done in copper plating) only an infinitesimal electromotive force is required to start the deposition; but the solution around the cathode soon becomes less concentrated in copper, producing a concentration-cell with an electromotive force opposite to that applied. This back electromotive force would evidently be diminished by decreasing the current-density, by agitating the whole solution, or by rotating the electrodes.

When a gas, such as hydrogen or oxygen, is set free at an electrode, a phenomenon, known as *gas-polarization*, is observed which does not occur in the deposition of metals. For when a gas is involved in the electrode-reaction its partial pressure determines the electrode-potential. Hence in a cell exposed to the air a slow, continuous electrolysis may take place before the applied electromotive force equals the electromotive force of the cell when the gas-pressure is one atmosphere; for the gas-forming substance is produced on the electrode at a lower pressure and is dissolved in the solution and carried away by convection and diffusion. Moreover, a sudden increase in the rate of electrolysis does not take place when the applied electromotive force is increased beyond that corresponding to a pressure of one atmosphere; for the gas-forming substance then passes into the electrode at this higher pressure, producing a supersaturated

adsorbed layer on its surface or a supersaturated solid solution within the metal from which the gas does not escape rapidly enough to reduce the effective pressure to one atmosphere. There is thereby produced a *back electromotive force* which is equal to the electromotive force of a voltaic cell in which the gas has this higher pressure, and which is larger than the electromotive force of a similar cell in which the gas has the partial pressure that prevails above the solution. The amount by which the back electromotive force exceeds the theoretical electromotive force at the prevailing partial pressure is called the *polarization* or *overvoltage*.

It will thus be seen that the applied electromotive force may be considered resolved into three parts: one equal to the minimum decomposition-potential or to the theoretical electromotive force of the resulting voltaic cell at the prevailing partial pressures; a second part equal to the polarization; and a third part, that uncompensated by the back electromotive force resulting from these two effects, and therefore available for forcing a current through the cell in accordance with Ohm's law. These considerations are illustrated by Prob. 84.

These principles suffice to enable the phenomena of polarization to be treated from experimental and thermodynamic standpoints. The various hypotheses that have been proposed in regard to the molecular mechanism by which gas-polarization results can not be here considered. These hypotheses involve considerations relating to surface-tension, adsorption, formation of unstable compounds, and rate of reaction in solid phases.

The back electromotive force produced by the electrolysis may be experimentally determined in the following ways:

- (1) By the method described in Prob. 84.
- (2) By finding the smallest value of the applied electromotive force at which bubbles form slowly but continuously at the electrode surface (this giving a value corresponding practically to a minimum current-density).
- (3) By applying a definite electromotive force to the cell long enough to charge the electrodes with the decomposition-products and then short-circuiting the electrodes through a high-resistance potentiometer, the applied potential being at the same time removed. From the so-measured back electromotive force the

overvoltage is obtained by subtracting the theoretical electromotive force corresponding to the prevailing gas-pressure, which is usually about one atmosphere.

Prob. 84. — Gas-Polarization. — Electromotive forces successively increasing in magnitude were applied at 22° to an electrolytic cell consisting of a large, unpolarizable, platinized platinum plate as anode, a small mercury surface as cathode, and a 0.1 wf. H_2SO_4 solution as electrolyte. Hydrogen gas at 1 atm. was bubbled steadily through the cell, and a resistance of 100,000 ohms was placed in series with it, the resistance of the cell being negligible in comparison. The current-strengths in millionths of an ampere corresponding to various applied electromotive forces in volts were as follows:

Current-strength	0.06	0.44	1.20	2.20	3.70	4.82
Applied electromotive force	0.32	0.48	0.62	0.77	0.95	1.08

a. Plot these current-strengths as ordinates against the electromotive forces as abscissas. *b.* Calculate the back electromotive force and polarization corresponding to each of these applied electromotive forces, tabulate these values, and plot the current-strengths against them on the same diagram. *c.* Calculate the effective pressure of the hydrogen at the electrode corresponding to the smallest of these back electromotive forces, assuming the logarithmic relation valid for perfect gases to hold up to this pressure.

The overvoltage is always found to increase with increase of the applied electromotive force and of the current-density; but it varies in a highly specific way with the chemical nature of the gas and with the chemical nature and physical state of the metallic electrode. Thus in certain experiments made with 1 normal H_2SO_4 the overvoltage of the hydrogen was found to have the following values:

	<i>Small Current-Density</i>	<i>Large Current-Density</i>
Platinized platinum	0.00 volt	0.07 volt
Smooth platinum	0.03	0.65
Lead	0.36	1.23
Mercury	0.44	1.30

In certain experiments with 2 normal KOH solution with a moderate current-density the overvoltage of the oxygen was

found at the start to be 0.44 volt on platinized platinum, 0.84 volt on smooth platinum, and 0.50 volt on iron; the value increasing to 1.46 on smooth platinum and to 0.59 on iron after two hours' passage of the current.

The phenomenon of gas-polarization and the overvoltage attending it are of great significance in technical processes. The overvoltage may greatly diminish the energy-efficiency of the process, the *energy-efficiency* being the ratio of the minimum electrical energy theoretically required to produce a definite quantity of some product of the electrolysis to the energy actually expended. Overvoltage may also make processes practicable which would otherwise not be possible; thus in charging a lead storage-cell hydrogen is not set free at the lead owing to its overvoltage, although the potential of the half-cell $\text{H}_2(1 \text{ atm.})$, $\text{H}_2\text{SO}_4 \cdot 20\text{H}_2\text{O}$ is about 0.4 volt less than that of the half-cell $\text{Pb} + \text{PbSO}_4(\text{s})$, $\text{H}_2\text{SO}_4 \cdot 20\text{H}_2\text{O}$.

Prob. 85. — Energy-Efficiency and Overvoltage. — In a certain commercial alkali-chlorine cell sodium hydroxide and chlorine are produced at an iron cathode and graphite anode, respectively, by the continuous electrolysis of a 25% NaCl solution which is slowly flowed through a diaphragm from the anode to the cathode compartment (to prevent the hydroxide-ion from migrating to the anode). In a certain case 4.5 volts were applied to the cell, whose resistance was 0.00080 ohm, yielding a current of 2000 amperes; and there flowed off each hour from the cathode 27,460 g. of solution containing 10% of NaOH and 13% of NaCl. The electromotive force of the voltaic cell $\text{H}_2(1 \text{ atm.})$, $\text{NaOH}(10\%) + \text{NaCl}(13\%)$, $\text{NaCl}(25\%)$, $\text{Cl}_2(1 \text{ atm.})$ has been independently determined to be 2.3 volts. *a.* Calculate the current-efficiency in the production of the sodium hydroxide. *b.* Calculate the energy-efficiency of its production. *c.* Calculate the voltage used to produce the current and that used to overcome the polarization, and tabulate these together with the minimum decomposition-potential. *Ans. b, 47.0%.*

IX. THE EFFECT OF TEMPERATURE ON THE
ELECTROMOTIVE FORCE OF
VOLTAIC CELLS.

43. The Effect of Temperature on the Electromotive Force of Voltaic Cells. — By substituting in the second-law free-energy equations (II, 32) the quantity ENF , which represents the free-energy decrease attending any change in state taking place reversibly in a voltaic cell, there result the following expressions, known as the *Gibbs-Helmholtz equation* (1878–82), for the effect of temperature on the electromotive force of voltaic cells:

$$N F \frac{dE}{dT} = \frac{\Delta H + ENF}{T}; \quad \text{or} \quad N F d\left(\frac{E}{T}\right) = \frac{\Delta H}{T^2} dT. \quad (70)$$

In this equation ΔH denotes the increase in heat-content which attends the change in state that takes place when N faradays of electricity flow through a cell of electromotive force E containing infinite quantities of the constituent substances.

Effect of Temperature on Electromotive Force.

Prob. 86. — Show from the Gibbs-Helmholtz equation under what conditions the electromotive force of a cell, a , is independent of the temperature; b , is proportional to the absolute temperature; c , increases with rising temperature; d , decreases with rising temperature.

Prob. 87. — a . Calculate the temperature-coefficient at 25° of the electromotive force of the cell $\text{H}_2(1 \text{ atm.}), \text{H}_2\text{SO}_4(0.01 \text{ wf.}), \text{O}_2(1 \text{ atm.})$, which was found in Prob. 38 (V, 29) to be 1.228 volts. The heat-content of $1\text{H}_2\text{O}(l)$ is $-68,370 \text{ cal.}$ b . Calculate the electromotive force of this cell at 0° , assuming that the heat-content increase attending the change in state does not vary appreciably between 0 and 25° .

Prob. 88. — Calculate the temperature-coefficient at 25° of the electromotive force (1.262 volts) of the cell $\text{H}_2(1 \text{ atm.}), \text{HCl}(4 \text{ wf.}), \text{Cl}_2(1 \text{ atm.})$ from the heat-content ($-22,060 \text{ cal.}$) of $1\text{HCl}(g)$ and its *partial* heat of solution ($-16,000 \text{ cal.}$) in 4 wf. HCl solution.

**** Prob. 89.** — Calculate the electromotive force at 40° of the storage-cell $\text{Pb}(s) + \text{PbSO}_4(s), \text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}, \text{PbSO}_4(s) + \text{PbO}_2(s)$, from its electromotive force (2.096 volts) at 0° and the heat data given in Prob. 64 (IV, 40).

Prob. 90. — *Calculation of Heat of Reaction.* — The cell $\text{Ag}(s) + \text{AgCl}(s), \text{HCl}(1 \text{ wf.}), \text{Hg}_2\text{Cl}_2(s) + \text{Hg}(l)$ has at 15° and

at 35° an electromotive force of 0.04204 volt and 0.04880 volt, respectively. *a.* Formulate the change in state that takes place in the cell per faraday which passes through it. *b.* Calculate the attendant increase in entropy ΔS , in free energy ΔF , and in heat-content ΔH at 25° .

**** Prob. 91. — *The Effect of Temperature on Electrode-Potentials.*** — *a.* Specify precisely the change in state whose heat-content increase would be used in calculating the temperature-coefficient of the molal electrode-potential of $\text{Zn(s)}, \text{Zn}^{++}$. *b.* Calculate the temperature-coefficient at 25° of this potential (0.758 volt) from the heat-content ($-95,500$ cal.) of $1\text{ZnCl}_2(\text{s})$, that ($-22,060$ cal.) of 1HCl(g) , and the heats of solution of these substances recorded in *II, 12*.



PART III.

THE RATE AND EQUILIBRIUM OF CHEMICAL CHANGES FROM MASS-ACTION AND PHASE VIEW-POINTS

CHAPTER VI

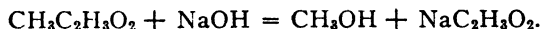
THE RATE OF CHEMICAL CHANGES

I. GENERAL PRINCIPLES AS TO THE RATE OF ISOTHERMAL HOMOGENEOUS REACTIONS.

1. The Mass-Action Law of Reaction-Rate. — The branch of chemistry concerned with the rate of chemical reactions is often called *chemical kinetics*.

The rate of a *homogeneous* chemical reaction (that is, of one taking place in a system consisting of a single phase) involving dissolved or gaseous substances may be defined to be the infinitesimal decrease $-dc_A$ in the concentration of one of the reactants A in an infinitesimal time dt divided by that time.

Prob. 1. — The Concept of Reaction-Rate. — Sodium hydroxide and methyl acetate in dilute aqueous solution react with each other, as expressed by the equation:



Starting with a solution 0.01 weight-normal (wn.) in methyl acetate and sodium hydroxide and keeping the temperature constant at 25°, the concentrations of the methyl alcohol and sodium acetate (in milli-equivalents per 1000 g. of water) after various times (in minutes) are found to be as follows:

Time	0	2	5	10	20	40	∞
Concentration	0	1.91	3.70	5.41	7.02	8.25	10.00

a. Plot these concentrations as ordinates against the times as abscissas. *b.* Determine from the plot the reaction-rate at the start, after 10 minutes, and after 30 minutes, stating the units in which the reaction-rate is expressed. *c.* Suggest an analytical method by which the rate of this reaction could be followed experimentally.

The effect of concentration on the rate of chemical changes has been found to be expressed by the following principle, known as the *mass-action law of reaction-rate*. The rate at any definite moment of a chemical reaction which takes place at a constant temperature between perfect solutes or between perfect gases is proportional to the prevailing concentration of each of the reacting substances raised to a power equal to the number

of molecules of that substance which actually take part in the molecular process by which the reaction occurs. Thus the rate of a reaction step whose molecular process is that given by the chemical equation $aA + bB + \dots = eE + fF + \dots$ is expressed by either of the differential equations: *

$$-\frac{dc_A}{dt} = k c_A^a c_B^b \dots; \quad \text{or} \quad -\frac{dc_B}{dt} = k' c_A^a c_B^b \dots. \quad (1)$$

The choice of the reactant, whose concentration change is to be considered, is optional; but it may be noted that the proportionality constants k and k' are related by the simple proportion $k/k' = a/b$.

The proportionality-constant k or k' which occurs in the rate equation selected is called the *specific reaction-rate*. It evidently represents the actual rate which the reaction would have, under the assumption of proportionality, if the concentration of each of the reactants were unity. Its numerical value depends not only on the units of concentration and time employed, but also on the particular reactant (or reaction-product) selected in formulating the differential equation expressing the rate. In this matter there is, however, little uniformity of usage. The concentration is conveniently expressed in mols per liter or sometimes (in the case of aqueous solutions) in mols per kilogram of solvent; and the time is most commonly expressed in minutes or hours depending on the rate of the reaction.

The law is exact only for perfect gases and perfect solutes; but, like other such laws, it holds true approximately up to moderate concentrations. It may be derived from kinetic considerations (III, 16) under the assumption that reaction can take place only when a molecules of A collide with b molecules of B. The large effect of temperature on reaction-rate (VI, 16) indicates that for slow reactions only a small fraction of such collisions result in reaction.

To formulate correctly the law of the rate of any definite reaction, it is essential, as implied above, to know the molecular process, commonly called the *reaction-mechanism*, by which the resultant reaction is actually brought about. Thus it is essential

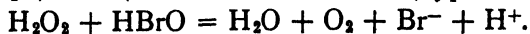
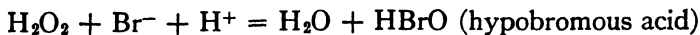
* It may obviously be equally well expressed by either of the equations:

$$dc_B/dt = k'' c_A^a c_B^b; \quad \text{or} \quad dc_F/dt = k''' c_A^a c_B^b.$$

to know whether the whole reaction is the result of a single chemical change (and if so, just what kinds of molecules are involved in it), or whether the reaction is the result of a succession of chemical changes (and if so, which of these take place so slowly as to have appreciable effects in determining its rate). Two illustrations of the bearing of mechanism on reaction-rate may be presented.

Consider first the reaction $2\text{CH}_3(\text{C}_2\text{H}_3\text{O}_2)$ (methyl acetate) + $\text{Ba}(\text{OH})_2 = 2\text{CH}_3\text{OH} + \text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ taking place in aqueous solution. If the law of reaction-rate were formulated in accordance with this equation, the rate would evidently be placed proportional to the square of the concentration of the methyl acetate and to the first power of that of the barium hydroxide. The ionic theory has shown, however, that barium hydroxide exists in aqueous solutions in the form of its ions; and this indicates that the decomposition of the ester is actually brought about by hydroxide-ion, in accordance with the mechanism $\text{CH}_3(\text{C}_2\text{H}_3\text{O}_2) + \text{OH}^- = \text{CH}_3\text{OH} + \text{C}_2\text{H}_3\text{O}_2^-$. If this is the case, the rate will be proportional to the first power of the concentration of the ester, as well as to that of the hydroxide-ion (or of the base itself); and this has been proved to be true by direct measurements. It will be noted that this obvious interpretation of the mechanism would have been impossible before the development of the ionic theory.

Consider secondly the resultant reaction $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ taking place in an aqueous solution of hydrobromic acid. The rate of this reaction might from the equation be expected to be proportional to the second power of the concentration of the hydrogen peroxide. Yet it is found experimentally to be proportional to the first power of this concentration, and also to be proportional to the concentration of hydrogen-ion and to that of bromide-ion in the solution, even though these substances do not appear in the equation expressing the resultant reaction. These experimental results are, however, fully accounted for by the mechanism of the reaction; for this has been shown (*Bray, Livingston, 1923*) to take place in the two successive stages expressed by the equations:



The second of these reactions is so rapid that any HBrO produced by the first reaction is almost instantly destroyed, with the consequence that the rate of the first reaction determines the resultant decomposition of the peroxide, and that this takes place in accordance with the law predicted from the first equation.

Since the mass-action law of reaction-rate (unlike the mass-action law of equilibrium) can be formulated only when the mechanism by which the reaction takes place is known, it is only in simple cases, where the mechanism is clearly indicated, that it is possible to predict the relation between the rate of the resultant reaction and the concentrations of the substances involved in it. This relation therefore must often be experimentally determined by reaction-rate measurements. Then conversely, from the so-established relation, with the aid of the law of reaction-rate, conclusions may be drawn as to the mechanism of the reaction. And it may be stated in advance that the relation between reaction-rate and concentrations, and therefore presumably that the reaction-mechanism, often proves to be much simpler than corresponds to the chemical equation expressing the resultant reaction.

2. Formulation of the Law of Reaction-Rate for Various Types of Reactions. The Order of the Reaction-Rate. — As stated above, the form of the law applicable to any definite reaction-rate must, except in the case of simple reactions, be determined experimentally. The procedure consists in determining the power of the concentration of each substance to which the actual rate is proportional. It is therefore desirable first to formulate the various forms of the differential equation (Eq. 1) and the corresponding integrated expressions that are applicable to the simpler types of reaction. For gaseous reactions taking place at constant pressure, the volume of the reacting mixture often changes as the reaction progresses, producing thereby a corresponding change in the concentrations of the reactants which must be taken into consideration in formulating the differential reaction-rate equations. No such complication arises in the case of reactions involving solutes, since the volume of the solution remains substantially constant; and in the case of gaseous reactions it may be avoided by measuring the rate at constant volume.

Reaction-rates that are expressed by a differential equation which contains only the first power of the concentration of a single substance are said to be of the *first-order*. Reaction-rates which are proportional to the concentrations of each of two substances or to the square of the concentration of a single substance are said to be of the *second-order*. And in general, the *order of a reaction-rate* is said to be equal to the sum of the powers of the concentrations in the differential equation expressing the rate.

First-Order Reaction-Rates.

Prob. 2. — The hydrolysis (splitting by water) of sucrose (cane-sugar) in dilute acid solutions is expressed by the equation: $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{sucrose}) + \text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6(\text{glucose}) + \text{C}_6\text{H}_{12}\text{O}_6(\text{fructose})$. The rate of this reaction at a constant temperature in the presence of a definite concentration of a definite acid is found to be proportional to the concentration of the sucrose. *a.* Formulate the differential equation expressing this reaction-rate, representing by c the sucrose concentration at any time t . *b.* Integrate this equation between the time limits 0 and t and the corresponding concentration limits, representing the initial sucrose concentration by c_0 .

Prob. 3. — In a solution containing 0.3 mol of cane-sugar and 0.1 mol of HCl in 1000 g. of water, it is found (by measuring with a polarimeter the change in the optical rotatory power) that 32% of the sugar is hydrolyzed at 48° in 20 minutes. *a.* Calculate the specific reaction-rate and the actual rates at the beginning and at the expiration of 20 minutes. *b.* Calculate the percentage of sugar hydrolyzed after 40 minutes.

Second-Order Reaction-Rates.

Prob. 4. — *a.* Formulate the differential equation expressing the rate in dilute aqueous solution of the reaction between methyl acetate A and sodium hydroxide B in terms of the concentrations c_A and c_B of these reactants at any time t . *b.* Integrate this equation between the time limits 0 and t (1) for the case that the initial molal concentrations c_{A0} and c_{B0} are the same, and hence at all stages $c_B = c_A$; and (2) for the case that the initial molal concentration c_{B0} of the base exceeds that c_{A0} of the ester by a fixed amount d , and hence at all stages $c_B = c_A + d$. (Refer to a table of integrals, if preferred.)

Prob. 5. — When 0.01 mol of methyl acetate and 0.01 mol of NaOH are dissolved at 25° in 1000 g. of water, 11.8% of the ester is decomposed per minute at the start. *a.* Calculate the

time required for one half of the ester in this mixture to be decomposed. *b.* Calculate the time required for this decomposition when 0.01 mol of methyl acetate and 0.02 mol of NaOH are dissolved in 1000 g. of water. *Ans. b, 3.4 min.*

Expressions can be similarly derived for *reaction-rates of the third order*; that is, for rates that are proportional to the concentration of each of three substances, or to the concentration of one substance and the square of the concentration of a second substance, or to the cube of the concentration of one substance.

For certain types of reaction, which take place at constant volume, there are summarized in Table I the integrated expressions for the reaction-rate in terms of the molal concentrations c_0 and c at the time zero and the time t , and in terms of the fraction x of the reactants transformed at the time t .

TABLE I. EXPRESSIONS FOR THE REACTION-RATE OF TYPICAL REACTIONS.

Order	Type of Reaction	Integrated Expressions	
		In Terms of c_0 and c	In Terms of c_0 and x
First	$A = eE + \dots$	$\ln \frac{c_0}{c} = k_1 t \quad (2)$	$\ln \frac{1}{1-x} = k_1 t \quad (6)$
Second	$2A = eE + \dots$; or $A + B = eE + \dots$; for $c_A = c_B = c$	$\frac{1}{c} - \frac{1}{c_0} = k_2 t \quad (3)$	$\frac{x}{1-x} = k_2 c_0 t \quad (7)$
Third	$3A = eE + \dots$; or $A + B + C = eE + \dots$; for $c_A = c_B = c_C = c$	$\frac{1}{c^2} - \frac{1}{c_0^2} = 2 k_3 t \quad (4)$	$\frac{x(2-x)}{(1-x)^2} = 2 k_3 c_0^2 t \quad (8)$
Third	$A + 2B = eE + \dots$; for $c_B = 2 c_A$ (or for equivalent quantities present at the start)	$\frac{1}{c_A^2} - \frac{1}{c_{A0}^2} = 8 k_3 t$; or $\frac{1}{c_B^2} - \frac{1}{c_{B0}^2} = k_3' t \quad (5)$	$\frac{x(2-x)}{(1-x)^2} = 8 k_3 c_{A0}^2 t$ where $1-x = c_A/c_{A0}$; or $\frac{x'(2-x')}{(1-x')^2} = k_3' c_{B0}^2 t \quad (9)$ where $1-x' = c_B/c_{B0}$

Prob. 6. — Third-Order Reaction Rates. — Derive Eqs. 5 and 9 from the differential equations expressing the mass-action law of reaction-rate for the type of reaction involved.

From Eqs. 6–9 two special principles may be deduced which furnish simple means for determining the ratio of the specific rates of the same reaction at two temperatures or of two analogous reactions at the same temperature, and for determining the order of any definite reaction.

Specific Reaction-Rate in Relation to Time of Transformation.

Prob. 7. — Consider two experiments upon the rates of the same reaction at two different temperatures, or upon the rates of two different reactions of the same order at the same temperature, in which the initial concentrations are the same; and show how the times t' and t'' required for transforming any definite fraction (such as 20%) of the reactants are related to the specific reaction-rates k' and k'' , a , for a second-order rate, b , for a third-order rate.

Prob. 8. — At 25° the specific rate of the reaction between sodium hydroxide and methyl acetate is 1.8 times as great as that of the reaction between sodium hydroxide and ethyl acetate. Find the ratio of the times required for decomposing 90% of the two esters when equivalent quantities are present at the start.

Effect of the Volume of the Reacting Mixture on the Time of Transformation.

Prob. 9. — Show in the case of a reaction taking place between definite quantities of the reactants at a definite temperature and at a constant volume v how the time t_1 , t_2 , or t_3 required for transforming a definite fraction of the reactants varies with that volume v when the reaction-rate is, a , of the first order; b , of the second order; c , of the third order.

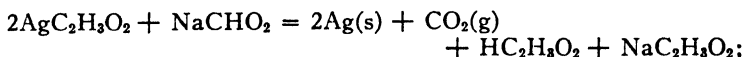
Prob. 10. — Show from the above expressions how the time required for the transformation of any definite fraction of a definite quantity of the reacting substances would vary if the quantity of solvent in which they are dissolved were increased ten-fold, a , in the case of the cane-sugar hydrolysis; b , in the case of the decomposition of methyl acetate by sodium hydroxide.

3. Experimental Determination of the Law of Reaction-Rates and of their Mechanism. — To determine the law expressing the effect of the concentrations of the reactants on the rate of any definite reaction, and therefore to determine the order of

its reaction-rate, two different experimental methods may be employed.

In one of these methods the fractions of the reactants transformed at various times throughout the course of a single reaction-rate experiment are measured, the corresponding values of the specific reaction-rates are calculated for the three orders by Eqs. 6-9, and the three series are compared to determine which equation leads to the most constant values. In the second method (illustrated in principle by Probs. 9 and 10) there are carried out a number of separate reaction-rate experiments in which the initial concentrations of the reactants are varied, in each case the fraction transformed after a definite time is measured, and the specific reaction-rates corresponding to the different orders are calculated and compared. The first of these methods is satisfactory when the reaction-rate is not influenced by the reaction-products nor complicated by the occurrence of side reactions. But because of the frequency of such effects the second method is in general much more reliable. The results obtained by this method can be made especially significant by varying the initial concentrations widely and by measuring the times that are required for only a small part (10-20%) of the total transformation to take place, so that the reaction-products may be present only in small proportion.

Prob. 11. — Determination of the Order of a Reaction. — In aqueous solution at 100° silver acetate has been found (Noyes, Cottle, 1898) to react slowly with sodium formate as follows:



the underlying ionic reaction being $2\text{Ag}^+ + \text{CHO}_2^- \rightleftharpoons 2\text{Ag(s)} + \text{CO}_2\text{(g)} + \text{H}^+$. *a.* In one experiment 0.2 wf. $\text{AgC}_2\text{H}_3\text{O}_2$ was mixed at 100° with an equal volume of 0.1 wf. NaCHO_2 (producing a solution 0.1 wn. in each); and after definite intervals of time samples were removed and the concentration of undecomposed silver salt was determined by titration with potassium thiocyanate. It was found to be 0.0670 wn. after 2 minutes, 0.0468 wn. after 6 minutes, and 0.0323 wn. after 14 minutes. By calculating the specific reaction-rates show whether these data conform more closely with a second-order or with a third-order reaction-rate. *b.* Another experiment was made in which the initial concentrations of $\text{AgC}_2\text{H}_3\text{O}_2$ and NaCHO_2 were 0.05 wf. and 0.025 wf.,

respectively (each being 0.05 wn.); and it was found that the silver salt concentration was 0.0316 wn. after 8 minutes. Calculate the specific reaction-rate, and compare it with the one for the two-minute period in Expt. *a*, so as to show to which order these results most closely conform. *Ans. a.* Second order, 2.46, 1.89, 1.50; third order, 61, 59, 61. *b.* Second order, 1.46, 2.46; third order, 75, 61.

There is a distinction between the order of the rate of a reaction and its mechanism. The order expresses an experimentally determined law of the resultant reaction-rate. The mechanism, though it must be consistent with the order, often involves hypothetical considerations as to the chemical reactions that are actually taking place. With respect to its mechanism a single reaction is said to be *unimolecular*, *bimolecular*, or *trimolecular*, according as one, two, or three molecules take part in the molecular process by which the rate of the reaction is considered to be determined.

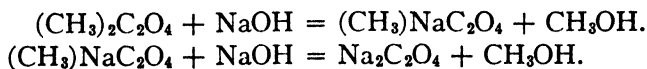
Since the mechanism must be studied in detail for each reaction or type of reaction, little of a general character can be said about it. Its further consideration is therefore postponed to the following sections where various types of reactions are discussed.

4. Independent or Consecutive Reactions Taking Place Simultaneously. — It often happens that two or more related reactions are taking place simultaneously. Some of the important types of such reactions are the following.

(1) A substance may be undergoing change in two different senses; thus, in the presence of iodine which acts as a catalyst, chlorbenzene and chlorine in carbon bisulfide solution undergo the two independent reactions represented by the equations:



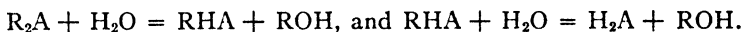
(2) The products resulting from one reaction may undergo change by a second reaction; thus, when dimethyl oxalate and sodium hydroxide are brought together in aqueous solution, the following reactions take place consecutively:



In the case of such reactions taking place simultaneously, the rate of each is determined by its own specific reaction-rate and by the concentrations of the substances involved in it, just as if the other reaction were not taking place. In accordance with this *law of independence of reaction-rates* the differential equations expressing the rates can be formulated.

Prob. 12. — Formulation of the Rates of Independent Simultaneous Reactions. — Calculate the specific reaction-rates k_1 and k_2 of the two reactions considered in case (1) above, supposing that at some definite temperature and with a definite iodine concentration it were found that in a CS_2 solution initially 0.5 wf. in $\text{C}_6\text{H}_5\text{Cl}$ and 0.5 wf. in Cl_2 15% of the $\text{C}_6\text{H}_5\text{Cl}$ is converted into ortho $\text{C}_6\text{H}_4\text{Cl}_2$ and 25% into para $\text{C}_6\text{H}_4\text{Cl}_2$ in 30 minutes. *Ans.* $k_1 = 0.0167$; $k_2 = 0.0278$.

Prob. 13. — Formulation of the Rates of Consecutive Simultaneous Reactions. — An ester R_2A (such as dimethyl succinate, $\text{CO}_2\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{CH}_3$) of a slightly ionized dibasic acid H_2A in an aqueous solution of definite hydrogen-ion concentration (as in 0.1 n. HCl) gradually undergoes complete hydrolysis in two consecutive stages by the following reactions:



Denoting the specific rates of these reactions by k_1 and k_2 , the initial molal concentration of the ester R_2A by c_0 and the molal concentration at any time t of R_2A , RHA , and H_2A by c , c' , and c'' , respectively, formulate differential expressions for the (resultant) rates at which c and at which c' decrease.

Note. — Two independent differential equations are thus obtained which may be solved for the concentrations c and c' by carrying out the mathematical operations. The results are as follows:

$$c = c_0 e^{-k_1 t}; \quad c' = c_0 \frac{k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}).$$

The rate of such hydrolytic reactions has been experimentally followed by titrating after definite intervals of time the acid produced, whose normality evidently equals the mols of RHA plus twice the mols of H_2A present per liter. The value of the specific reaction-rate k_2 was then simply determined by measuring the rate in separate experiments in which the half-ester RHA was alone present at the start. And by combination of the results of the two series of experiments, with the aid of the theoretical equations, the value of the other specific reaction-rate k_1 was derived (*Meyer, 1909*).

5. Opposing Reactions Taking Place Simultaneously and the Relation of their Rates to the Equilibrium Conditions. —

The products of a chemical change may react with one another in the reverse direction, so that the two opposing reactions are taking place simultaneously. Thus hydrogen, iodine, and hydrogen iodide, in the gaseous state, undergo a resultant reaction in the one or the other of the two opposing directions, depending on the concentrations of the respective substances, and the mechanisms of the two reactions have been shown to be expressed by the following equations:



The rate of the resultant reaction in such a case may be formulated, with the aid of the law of the independence of reaction-rates, in terms of the concentrations and the two specific reaction-rates k_1 and k_2 . In order to avoid ambiguity in regard to the values of k_1 and k_2 , it is most convenient to formulate both for the direct and for the opposing reaction a differential expression for the rate of change with time of the molal concentration of the same one of the different possible molecular species, and to combine these equations so as to obtain an expression for the resultant reaction rate.

Prob. 14. — Resultant Rate of Two Opposing Reactions. —

a. Formulate an expression for the resultant rate at which hydrogen iodide is produced in a gaseous mixture of hydrogen, iodine, and hydrogen iodide, in terms of the molal concentrations (H_2), (I_2), and (HI) of these substances prevailing at any time t . *b.* Formulate a corresponding expression in terms of the initial molal concentrations, A , B , and E , of these substances and of the increase y in the molal concentration of HI that has taken place after any time t . *c.* Bring the last expression into a form in which it could be directly integrated with respect to the variables y and t .

Note. — The integrated form can then evidently be solved for the value of y at any time t , provided the two specific reaction-rates are known and the initial concentrations are specified.

Prob. 15. — Relation of the Equilibrium-Constant of the Resultant Reaction to the Specific Rates of the Opposing Reactions. —

a. Derive the equilibrium-constant K for the formation and decomposition of hydrogen-iodide from the expression obtained in Prob. 14*a*, noting that there will be equilibrium when the concen-

trations are such that the rates of the two opposing reactions become equal or when the rate of the resultant reaction becomes zero. *b.* Modify the expression formulated in Prob. 14*a* by eliminating one of the specific reaction-rates k_1 or k_2 and introducing the equilibrium-constant K .

Note.—It has been proved experimentally that the mechanisms of the two opposing reactions are actually those corresponding to the equations $H_2 + I_2 = 2HI$ and $2HI = H_2 + I_2$, and that the equilibrium-constant is equal to the ratio of the two specific reaction-rates. This was the result of a comprehensive research (*Bodenstein, 1899*) upon the rates and upon the equilibrium of this reaction in a variety of mixtures with different initial concentrations. In this research known quantities of hydrogen iodide were sealed in glass bulbs, these were heated for a definite length of time at some definite temperature (between 283° and 508°), and the bulbs were then cooled and opened, and their contents submitted to chemical analysis.

Consider now in general any reaction $aA + bB + \dots \rightleftharpoons eE + fF + \dots$ having a measured rate in both directions corresponding to the mechanisms indicated by this equation, and having therefore a resultant reaction-rate given by the expression,

$$\frac{d(E)}{dt} = k_1 (A)^a (B)^b \dots - k_2 (E)^e (F)^f \dots \quad (10)$$

Now the condition of equilibrium is that $d(E)/dt = 0$, and therefore that:

$$\frac{(E)^e (F)^f \dots}{(A)^a (B)^b \dots} = \frac{k_1}{k_2} = K, \text{ a constant.} \quad (11)$$

The constancy of this concentration-product is, however, the mass-action law of chemical equilibrium; and the constant itself is the equilibrium-constant of the reaction.

This result is of great importance, first because it furnishes a derivation of the law of chemical equilibrium, and secondly because it shows that the equilibrium-constant K is the ratio k_1/k_2 of the specific rates of the two opposing reactions. This interprets equilibrium not as a condition in which no change is taking place, but as one in which the two opposing reactions are taking place at equal rates.

Although the mass-action law of chemical equilibrium is here derived from the mass-action law of reaction-rate, an important difference between the two laws is to be noted. Namely, although the true expression for the rate of a reaction depends on its actual mechanism yet a correct expression is obtained for its equilibrium, quite irrespective of rate mechanism, by applying the mass-action law to the substances involved in any possible reaction.

II. HOMOGENEOUS REACTIONS BETWEEN DISSOLVED SUBSTANCES.

6. Hydrolysis of Organic Substances in the Presence of Acids. — Of very frequent occurrence and of great importance in the field of organic chemistry are the reactions in aqueous solutions called *hydrolytic reactions*, in which a molecule is hydrated and then split into two or more smaller molecules. The reactions usually require a measurable time for their occurrence, and take place at a rate proportional to the concentration of the substance undergoing hydrolysis. This has already been illustrated (VI, 1) in the case of sucrose. Innumerable other such reactions exist, however. Examples of various types are shown in Table II.

TABLE II. TYPICAL HYDROLYTIC RELATIONS.

<i>Substances</i>	<i>Typical Reaction</i>
Disaccharides *	$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$ (monosaccharides)
Starches †	$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$
Esters	$CH_3CO_2CH_3 + H_2O = CH_3CO_2H + CH_3OH$
Fats	$C_3H_5(C_{18}H_{35}O_2)_3 + 3H_2O = C_3H_5(OH)_3 + 3C_{18}H_{35}O_2$ (stearin) (glycerol) (stearic acid)
Amides	$CH_3CONH_2 + H_2O = CH_3CO_2H + NH_3$ $= CH_3CO_2^- + NH_4^+$
Anhydrides	$(CH_3CO)_2O + H_2O = 2CH_3CO_2H$
Proteins	$C_nH_bN_cO_d + nH_2O = \text{amino-acids } (NH_2CH_2CO_2H, \text{ etc.})$

* Some important disaccharides are: maltose, which yields only the monosaccharide glucose; sucrose, which yields two monosaccharides, glucose and fructose; and lactose (milk-sugar), which yields glucose and galactose (another monosaccharide).

† Thus starch and glycogen (animal starch) yield glucose; inulin yields fructose.

Most hydrolytic reactions take place with extreme slowness in pure water (except at high temperatures), but are greatly accelerated by the presence of acids; the rate being then approximately proportional to the concentration of the acid (when this is largely ionized). For example, the specific reaction-rate of the sucrose hydrolysis at 35° has been found to be 10.0 times as great in a 0.01 normal as it is in a 0.001 normal solution of hydrochloric acid. At higher acid concentrations or in the presence

of much neutral salt considerable deviations from proportionality exist; thus, the rate of the sucrose hydrolysis is 140 times as great in a 0.90 normal as in a 0.01 normal solution of hydrochloric acid (see Table III).

Partially ionized acids, such as sulfuric acid or acetic acid, produce at the same normal concentration a smaller rate of hydrolysis than do completely ionized acids, such as hydrochloric acid. Indeed, in general, acids give rise to rates which are approximately proportional to the hydrogen-ion concentrations in their solutions, up to moderate values of these concentrations. Thus the reaction-rates for the hydrolysis of sucrose at 0.15 molal and 35° in the presence of hydrochloric and acetic acids have been found (*Fales, Morrell, 1922*) to have relative values, referred to that in 0.001 normal hydrochloric acid as unity, as shown in Table III. The hydrogen-ion concentrations (H^+) are calculated by considering that the hydrochloric acid is completely ionized, and that the acetic acid has (at 35°) an ionization-constant of 0.000017.

The principle that the specific reaction-rate of hydrolytic reactions is proportional to the hydrogen-ion concentration has often been employed conversely for determining approximately the hydrogen-ion concentration in dilute solutions; for other kinds of ions at small concentrations (except hydroxide-ion) do not exert a large effect on the rate of such reactions.

TABLE III. RELATIVE RATES OF THE HYDROLYSIS OF SUCROSE BY ACIDS AT 35°.

<i>Acid</i>	<i>Normality</i>	$(H^+) \times 10^3$	<i>Relative Values of Reaction-Rate</i>
Hydrochloric	0.900	900.	1400.
	0.300	300.	353.
	0.100	100.	107.
	0.010	10.0	10.0
	0.001	1.00	1.00
Acetic	0.040	0.82	0.88
	0.008	0.36	0.35
	0.001	0.12	0.11

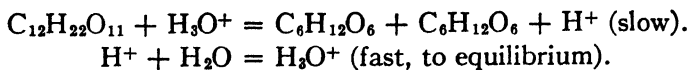
Prob. 16. — Determination of Hydrogen-Ion Concentration Through its Catalytic Effect. — Diazoacetic ester decomposes in

aqueous solution according to the equation $\text{CHN}_2 \cdot \text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O} = \text{CH}_2\text{OH} \cdot \text{CO}_2\text{C}_2\text{H}_5 + \text{N}_2$, and the reaction is catalyzed by hydrogen-ion. At 25° in a solution 0.1 weight-formal in acetic acid, whose ionization is 1.34%, it is found by measuring the nitrogen evolved that 37.5% of the ester is decomposed in 10 minutes. Assuming that it takes 67 minutes to decompose the same percentage of the ester in a solution 0.1 formal in sodium hydrogen tartrate, calculate the molality of hydrogen-ion in that solution.

7. Catalysis of Hydrolytic Reactions by Hydrogen-Ion.

— The effect of hydrogen-ion on hydrolytic reactions is an example of the important phenomenon of *catalysis*, a term used to denote the acceleration of a chemical reaction by the presence of a substance which is not itself consumed by the reaction. This term expresses an observed effect, and is used without reference to any theoretical explanation of the effect or to the mechanism of the reaction.

It is, however, of much interest to determine the mechanism of catalytic action wherever possible. Now, the catalysis of hydrolytic reactions has been proved in some cases, and is commonly assumed in other cases, to arise from the facts that the catalyst forms by reaction with one of the reactants an intermediate compound and that this then reacts with the second reactant more rapidly than does the first reactant and in such a way as to regenerate the catalyst. For example, the catalytic effect of hydrogen-ion may arise from its union with water to form the hydrated ion H_3O^+ in equilibrium proportions, and from the fact that this reacts with disaccharides, esters, etc., at a more rapid rate than does water itself. The mechanism of the sucrose catalysis, for example, would then be expressed by the two equations:



There is no independent evidence that this is the true mechanism of this type of hydrolysis; but the fact that the hydrolyses of the most varied substances are all catalyzed by hydrogen-ion shows that the water, not the substance undergoing hydrolysis, is activated in some way. Moreover, it is known from electrical transference experiments (*V*, 19) that hydrogen ions are hydrated

in aqueous solutions, and it is plausible that the water molecules attached to these ions may be more reactive than ordinary water molecules.

Prob. 17. — Catalysis of Hydrolytic Reactions by Hydrogen-Ion. — Show that the hypothetical mechanism of hydrolytic reactions suggested above explains the proportionality between the rate of hydrolysis of sucrose and the concentrations of sucrose and of hydrogen-ion, by formulating the equations expressing the conditions of equilibrium and the principle of reaction-rate involved.

8. Hydrolysis of Organic Substances in the Presence of Bases. — Almost all the types of hydrolytic reactions * listed in Table II take place in the presence of bases, as well as of acids, and often more rapidly with bases than with acids. Such reactions are therefore of great importance in organic chemistry.

The rate is found to be proportional to the hydroxide-ion concentration to which the base gives rise. Moreover, as the base is consumed by combining with the acid produced by the reaction, the decrease in the concentration of the base, as well as in that of the substance undergoing hydrolysis, has to be taken into account. The reaction is therefore of the second order, as shown by Probs. 4 and 5, which illustrate a reaction of this type.

Conversely, the relative rates of such hydrolytic reactions, especially of the saponification of esters, in a solution with known and in solutions with unknown hydroxide-ion concentration can be used for determining the concentration of this ion in the latter solutions.

Prob. 18. — Hydroxide-Ion Determination by Reaction-Rate Experiments. — Assuming the correctness of the suggested mechanism of the methyl acetate decomposition, determine the quantity of free NaOH present (because of hydrolysis) in a 0.1 wn. NaCN solution at 25° from the fact that at 25° the initial rate of decomposition of methyl acetate is 9.0 times as great in a solution 0.01 wn. in NaOH as in a solution 0.1 wn. in NaCN.

Some reactions of hydration (unaccompanied by splitting) are also greatly accelerated by hydroxide-ion. Thus milk-

* The reactions producing monosaccharides are complicated by the fact that these substances undergo a secondary decomposition with bases, especially when these are hot or concentrated.

sugar lactone $C_{12}H_{22}O_{11}$ dissolved in water changes its power of rotating polarized light owing to its partial conversion into the hydrate $C_{12}H_{22}O_{11} \cdot H_2O$; and the rate of this hydration, determined polarimetrically, has been found to be greatly increased by hydroxide-ion, which in this case acts as a catalyst. This reaction has also been employed for determining unknown hydroxide-ion concentrations.

9. Organic Reactions Catalyzed by Enzymes. — Certain complex colloidal substances, called *enzymes*, which are produced by animal and plant organisms, have a remarkable power of catalyzing certain organic reactions. The effect is highly specific, a particular enzyme being required for a particular reaction. Thus sucrase or invertase, an enzyme produced by the yeast plant, causes the conversion of sucrose into glucose and fructose; and xymase, another yeast enzyme, causes the conversion of glucose, but not of the analogous compound fructose, into ethyl alcohol and carbon dioxide. A very small quantity of enzyme suffices to decompose a very large quantity of the substance, showing that the enzyme is not consumed by the reaction.

Such reactions are of extraordinary importance in physiological processes. The following are some other examples of hydrolytic reactions caused by enzymes:

Fats (or other esters) + nH_2O (+ lipase) = fatty acids + glycerol.

Starch + nH_2O (+ amylase) = glucose.

Proteins + nH_2O (+ pepsin or trypsin) = proteoses, peptones, or poly peptides.

Polypeptides + nH_2O (+ erepsin) = amino-acids.

The following laws have been found to determine the action of the enzyme sucrase in causing the hydrolysis of sucrose into glucose and fructose:

The rate of hydrolysis is proportional to the (always relatively small) concentration of the enzyme.

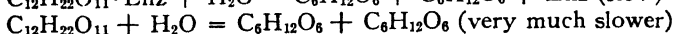
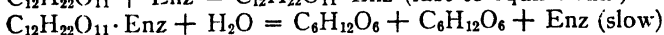
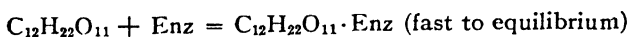
With increase in the concentration of the sucrose, the initial rate increases at first proportionally, and then more slowly; and at a moderate concentration (about 5% of sucrose) attains a maximum value, owing presumably to complete conversion of the enzyme into a sucrose-enzyme compound.

With still further increase in the concentration of sucrose the rate of hydrolysis decreases, owing probably to the fact that the activity or mass-action effect of the other reactant, the water, is then rapidly decreasing (*Nelson, Schubert, 1928*).

Investigations have indicated that the catalytic action of the enzyme is due to the formation of a compound with the substance undergoing decomposition (often called the *substrate*), and to the splitting of this compound into the cleavage-products of the substrate and into the original enzyme at a rate which is generally slow, yet is so much more rapid than the decomposition of the uncombined substrate that the latter is negligible.

The compound of the enzyme with the substrate is considered by some investigators (*Michaelis, Menten, 1931*) to be formed in true solution in accordance with the laws of mass-action, and by other investigators (*Nelson and others, 1916-7*) to be formed on the surface of the colloidal particles containing the enzyme in accordance with the laws of adsorption. Since both of these hypotheses assume the formation of a compound (either of the purely chemical or of the adsorption type) between the enzyme and substrate, either of them accounts for the qualitative phenomena of action of enzymes. Thus either hypothesis accounts for the facts, that the action, unlike that of hydrogen-ion, is specific with reference to the substance decomposed, and that the rate of decomposition is proportional to the concentration of enzyme, but attains a maximum value, corresponding to a saturation effect, as the concentration of the substrate is increased.

Prob. 19. — The Mechanism of Enzyme Action. — As stated above, the catalytic effect of the enzyme sucrase in the hydrolysis of sucrose may be explained by the following mechanism:



a. Show that at a fixed molal concentration (*S*) of sucrose the initial rate of hydrolysis is proportional to the relatively small total (or formal) concentration (ΣEnz) of sucrase. Note that the formal concentration of the enzyme is equal to the sum of the molal concentrations of its two forms as expressed by the equation, $(\Sigma \text{Enz}) = (\text{Enz}) + (\text{S} \cdot \text{Enz})$. *b.* By reference to the rate and equilibrium equations formulated in *a*, explain the facts enumer-

ated in the text; namely, that with a fixed concentration (Σ Enz) of sucrase but varying concentration (S) of sucrose, the initial rate of hydrolysis increases at first proportionally with the increasing sucrose concentration, then more slowly, attains a maximum value at a moderate sucrose concentration, and then decreases.

10. Reactions of Oxidation and Reduction and their Mechanisms. — A type of chemical change between inorganic substances which frequently requires measurable time for its occurrence is that of reactions of oxidation and reduction. For though the dissociation of molecules into ions and the union of ions with one another, which are usually alone involved in inorganic metathetical reactions, take place so rapidly as to be practically instantaneous, yet the transfer of electrons between atoms or atom-groups, which is involved in oxidation reactions, often requires amounts of time which vary within the widest limits.

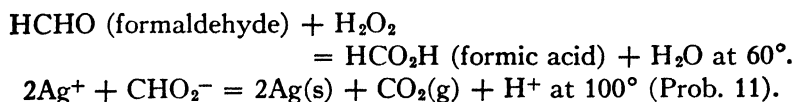
Three important types of oxidation-reactions may be distinguished:

1. Reactions which take place by a single molecular process corresponding to the equation expressing the resultant reaction.

2. Reactions which take place in successive stages, of which the first alone has a rate that is small enough to be measurable, and one that is not catalyzed by other substances.

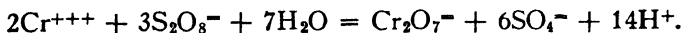
3. Reactions which take place in successive stages, the first of which involves the intermediation of a catalyst — a substance not involved in the resultant reaction.

1. Oxidation reactions which take place in aqueous solution at measurable rates that conform approximately to the law of reaction-rate in the form corresponding to the resultant reaction are illustrated by the following examples:

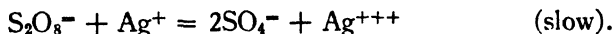


2. It is a frequent characteristic of inorganic oxidation reactions that the order of the reaction-rate is much lower than

3. An oxidation reaction is often caused to take place at a greatly increased rate (that is, is strongly catalyzed) by a substance not consumed by the reaction. To act as such a catalyst, a substance must apparently be itself capable of being oxidized or reduced by one reactant, and of being converted thereby to an oxidation-product or a reduction-product which is then restored to its original state of oxidation by the other reactant. For example, a chromic salt in acid solution might be oxidized to dichromate by peroxysulfate in accordance with the reaction:



This reaction, however, does not occur, either directly or in stages, when the substances involved in the reaction are alone present; but it does occur at a measurable rate when silver-ion is added at small concentration. This has been explained (*Yost, 1926*) by assuming that the reaction takes place in the two following stages:

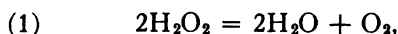


Prob. 20. — Catalysis of Oxidation Reactions. — a. Formulate the law which should express the rate of the oxidation of a chromic salt by peroxysulfate in the presence of silver-ion, assuming its mechanism to be that described in the above text. *b.* Explain how the rate of the reaction is related to the Cr^{+++} concentration. *c.* Assuming that a corresponding mechanism determines the rate of the reaction $\text{NH}_4^+ + 4\text{S}_2\text{O}_8^{--} + 3\text{H}_2\text{O} = \text{NO}_3^- + 8\text{SO}_4^{--} + 10\text{H}^+$ in the presence of Ag^+ , find the relative rates at which Cr^{+++} and NH_4^+ would be oxidized by $\text{S}_2\text{O}_8^{--}$ at a given concentration with Ag^+ ion also at a given concentration.

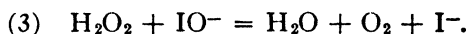
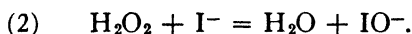
Note. — The various conclusions as to rates drawn in the preceding problem have been confirmed by experiment. Moreover, a solid basic sulfate of trivalent silver has been obtained by diluting a mixture of AgNO_3 , $\text{K}_2\text{S}_2\text{O}_8$, and H_2SO_4 .

Another example of catalytic oxidation in aqueous solution has already been cited in VI, 1, where the decomposition of hydrogen peroxide into water and oxygen in the presence of bromide-ion and hydrogen-ion was attributed to the slow conversion of these ions into HBrO by one H_2O_2 molecule, and the rapid reduction of this HBrO to H^+Br^- by a second H_2O_2 molecule.

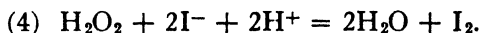
Another oxidation reaction whose catalytic mechanism has been well investigated is the decomposition of hydrogen peroxide into water and oxygen in the presence of iodide-ion. This decomposition in accordance with the equation,



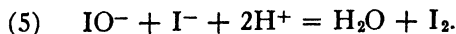
is very slow where the hydrogen peroxide is present alone, but becomes rapid in the presence of a moderate concentration of iodide-ion. The principles (considered in Probs. 21 and 22) determining the rate of the reaction seem to show that this catalytic effect is due to the occurrence of the reaction in the two stages represented by the equations:



In the presence of a considerable concentration of hydrogen-ion, as well as of iodide-ion, the hydrogen peroxide does not decompose to an important extent into water and oxygen in accordance with equation (1), but it yields water and iodine in accordance with the following equation:



The rate of this reaction is found, however, to be proportional to the iodide-ion concentration (not to its square) and to be dependent in only a secondary degree on the concentration of the hydrogen-ion. This can be accounted for by considering that reaction (4) takes place in two stages, namely, that represented by equation (2) above, and that represented by the following equation; this last reaction occurring almost instantaneously and completely when the hydrogen-ion concentration is large:



The Mechanism of Catalytic Oxidation.

Prob. 21. — State and formulate the principles that would express the rate of the decomposition of hydrogen peroxide in neutral solution in the presence of iodide-ion, assuming that it takes place, *a*, directly according to reaction (1); *b*, according to reactions (2) and (3), the latter taking place instantaneously; *c*, according to reactions (2) and (3), the IO^- produced by (2) soon

attaining such a concentration that reaction (3) thereafter takes place at the same rate as reaction (2). (Case *c* seems to represent what actually occurs.)

Prob. 22. — a. Show by reference to the equilibrium condition of reaction (5) why reaction (3), and therefore reaction (1), does not take place to any important extent in the presence of a considerable concentration of hydrogen-ion; also why reaction (5), and therefore reaction (4), does not take place to an important extent in a nearly neutral solution. *b.* Show what relative quantities of hydrogen peroxide would, if these explanations are correct, be decomposed per minute in a solution 0.1 formal in H_2O_2 and 0.1 formal in KI in the two cases that the solution is neutral and that it is moderately acid with HCl.

III. HOMOGENEOUS REACTIONS BETWEEN GASEOUS SUBSTANCES.

11. The Law of the Rate of Gaseous Reactions: Its Expression and Determination. — The mass-action law of reaction rate (VI, 1) applies to reactions involving gaseous substances, provided the reactions are truly homogeneous; that is, provided they take place only in the gaseous phase, and not, as is very often the case, on the walls of the vessel or on the surface of other solid substances with which the gas is in contact. Such acceleration of rate by a surface reaction is called *contact catalysis*.

The progress of gas reactions is usually followed by measuring the change in pressure of the gaseous mixture at a constant volume. It is therefore often convenient to replace the concentrations of the reacting substances by their partial pressures, which at constant temperature are proportional to the respective concentrations in the case of perfect gases, in virtue of the relations $p_A = c_A R T$, $p_B = c_B R T$, $\dots$. For example, the rate of the reaction $A + 2B = 2E$ (thus that of the reaction $O_2 + 2NO = 2NO_2$) at constant temperature may be expressed by the equation $-dp_A/dt = k p_A p_B^2$.

By replacing the partial-pressure decrease ($-dp_A$) by the appropriate multiple of the total-pressure change dp and introducing the initial pressures p_{A_0} , p_{B_0} , $\dots$, such equations may be brought into a form suitable for integration involving the pressures actually measured.

Similarly as with reactions in solutions, the differential equation expressing the rate of reaction between gases, and therefore the order of the reaction-rate, may be found in cases where complications do not arise from contact effects, or from the influence of the reaction-products, or from secondary reactions, by determining whether the integrated equation of the first, second, or some higher order best expresses the course of the reaction with a definite initial mixture. A much more reliable conclusion as to the law of the reaction-rate can, however, be reached by varying in separate experiments the initial pressures of the respective substances and determining the time required for a definite small fraction (for example, one fifth) to undergo reaction.

Prob. 23. — Law of the Reaction-Rate Determined by Varying the Initial Pressures. — By measuring the decrease in pressure at constant volume, the reaction $2\text{NO} + 2\text{H}_2 = \text{N}_2 + 2\text{H}_2\text{O}$ has been found (*Hinshelwood, Green, 1926*) to take place at 826° at the following rates. *a.* With equimolar quantities of NO and H_2 present, half of the gas reacted in 81 sec. when the initial total pressure was 708 mm., and in 224 sec. when it was 404 mm. Find the order of the reaction to which these data best conform. *b.* When the initial pressure of hydrogen was 400 mm. and the initial pressure of nitric oxide was (in three experiments) 359 mm., 300 mm., and 152 mm., the initial rate of decrease in total pressure (as determined by plotting the observed pressures against the times) was 1.50 mm., 1.03 mm., and 0.25 mm. per second, respectively. Determine from these data to what power of the partial pressures of nitric oxide the reaction-rate is proportional. *c.* When the initial pressure of nitric oxide was 400 mm. and the initial pressure of hydrogen was (in three experiments) 289 mm., 205 mm., and 147 mm., the initial rate of decrease in total pressure was 1.60 mm., 1.10 mm., and 0.79 mm. per second, respectively. Determine from these data to what power of the partial pressure of the hydrogen the reaction-rate is proportional. *d.* State what necessary conclusion as to the mechanism of the reaction can be drawn from these results; and suggest a definite mechanism that is consistent with this conclusion.

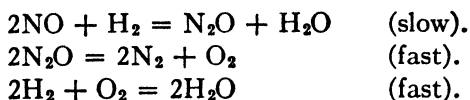
12. Gaseous Reactions Taking Place by a Single Molecular Process. — Only a comparatively small number of gas reactions have been found which proceed in accordance with the mass-action law corresponding to the resultant equation, without complications arising from contact-catalysis or from the occurrence of the reaction in successive steps. Two such reactions, namely $\text{H}_2 + \text{I}_2 = 2\text{HI}$ and $2\text{HI} = \text{H}_2 + \text{I}_2$, have already been discussed (VI, 5); and in Table IV (following Probs. 24 and 25) are listed some other reactions which are of this single type, at least within certain ranges of temperature and pressure.

Rate of the Reactions in the Arc Process of Nitrogen Fixation.

Prob. 24. — In the arc process of nitrogen-fixation air is brought in contact with an electric arc, the gas from the arc is rapidly cooled (by admixture with cold air and contact with the walls of the furnace), and under definite conditions the gas emerges from the furnace at 1250° and 1 atm. with a content of 2 mol-per-cent of nitric oxide (NO). Determine what percentage of this

trations of the reacting substances in ways that do not correspond to the number of molecules involved in the resultant reaction. Such apparent divergences can often be accounted for by assuming that the resultant reaction takes place in a series of successive reactions, that only one of these reactions takes place at a measurable rate, and that this rate determines the rate of the resultant reaction.

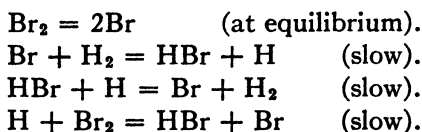
This is illustrated by the reaction $2\text{NO} + 2\text{H}_2 = \text{N}_2 + 2\text{H}_2\text{O}$. For the fact that its rate is found (Prob. 23) to be proportional to the square of the NO pressure and to the first power (not the square) of the H_2 pressure is plausibly explained by the following mechanism:



One of the best investigated rates of reaction, and one which illustrates a type of mechanism that is fairly common in the respect that it involves reactions with single atoms, is the rate of formation of hydrogen bromide from hydrogen and bromine gases at $225\text{--}300^\circ$. The resultant reaction is $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$, and this finally goes to completion at these temperatures. Its rate, however, has been found (*Bodenstein, Lind, 1906*) to be expressed, not by the corresponding simple differential equation, but by the equation:

$$\frac{d(\text{HBr})}{dt} = \frac{k(\text{H}_2)(\text{Br}_2)^{0.5}}{k' + (\text{HBr})/(\text{Br}_2)}.$$

This result was later interpreted (*Herzfeld, 1919*) by considering that the resultant reaction is brought about by the following mechanism:



Prob. 26. — Mechanism of the Hydrogen Bromide Formation. — Derive the above equation by proceeding as follows: Formulate a differential equation for the resultant rate by which

HBr is produced by the last three reactions. Find an expression for (H) by noting that the rate at which atomic hydrogen is produced by the second reaction must be substantially equal to the rate at which it is destroyed by the third and fourth reactions, inasmuch as the atomic hydrogen is known to be an intermediate that is always present at extremely small concentration. Substitute in the differential equation this expression for (H), and also an expression for (Br) obtained from the fact that the reaction $\text{Br}_2 = 2\text{Br}$ is at equilibrium; and simplify the resulting expression by transforming and assembling all the constants into two constants.

IV. EFFECT OF TEMPERATURE ON THE RATE OF HOMOGENEOUS REACTIONS.

14. General Principles as to the Effect of Temperature on Reaction-Rate. — Measurements of the change with the temperature of the rates of reactions taking place involving solutes or gases have shown that as a rule equal small increments of temperature cause an approximately equal multiplication of the specific rate of any definite reaction. Thus, if the specific rate of a reaction is increased 2.5 fold by raising the temperature from 0 to 10°, it will again be increased approximately 2.5 fold by raising the temperature from 10 to 20°. This principle and the order of magnitude of the deviations from it are illustrated by the following data for the first order decomposition of nitrogen pentoxide (*Daniels, Johnston, 1921*). The values k_2/k_1 are the ratios of the specific reaction rates at 10° intervals.

	25 to 15°	35 to 25°	45 to 35°	55 to 45°	65 to 55°
k_2/k_1	3.2	4.1	3.7	3.0	3.2

It has also been found that in the case of different reactions equal small increments of temperature cause not far from the same multiplication of their specific rates. Thus, a 10° rise of temperature multiplies the specific rate of the reaction between cane-sugar and water in the presence of acid 3.6 fold, that of gaseous iodine and hydrogen 1.6 fold, that of gaseous sulfur and hydrogen 2.2 fold, and the decomposition of azobenzene 1.9 fold.

A more general and more exact expression of the effect of temperature is that given by the following equations (*Arrhenius, 1889*), in which A is a constant for any definite reaction:

$$\frac{d \ln k}{dT} = \frac{A}{T^2}; \quad \text{or} \quad \ln \frac{k_2}{k_1} = A \frac{T_2 - T_1}{T_1 T_2}. \quad (12)$$

This expression is known as the *Arrhenius equation*. It is evident that $\ln k$ and $1/T$ will change proportionally in case the quantity A does not vary with the temperature. This conclusion has been experimentally confirmed in the case of many homogeneous reactions taking place both in the dissolved and the gaseous state. For example, a graph of the logarithms ($\ln k$) of the specific rates of the gaseous reaction $2\text{HI} = \text{H}_2 + \text{I}_2$ (as

derived from measured rate of decomposition corrected for the opposing reaction) plotted against the reciprocals ($1/T$) of the corresponding absolute temperatures is found within the experimental error to be a straight line, as required by the Arrhenius equation, even though the values of k vary from 0.00035 to 39, and the absolute temperatures vary from 556 to 781°.

Effect of Temperature on Reaction-Rate.

Prob. 27. — At 100° a certain reaction takes place to an extent of 25% in one hour. Estimate roughly how long it would take for the reaction to proceed to the same extent at 20°.

Prob. 28. — *a.* In a solution 0.01 molal in sodium hydroxide and 0.01 molal in ethyl acetate, 39% of the ethyl acetate is decomposed in 10 minutes at 25°, and 55% at 35°. Determine by the approximate principle how long it would take to decompose 55% at 15°. *b.* Calculate by the logarithmic equation how long it would take to decompose 50% of the ethyl acetate at 20°.

Prob. 29. — *a.* The decomposition of gaseous acetaldehyde into methane and carbon monoxide is represented by a second-order rate equation. At an initial concentration of 0.005 mol per liter, 27.6% decomposes in 300 seconds at 500° and 35.8% at 510°. Determine by the approximate principle how long it would take to decompose 35.8% at 490°. *b.* Calculate by the logarithmic equation how long it would take to decompose 30% of the acetaldehyde at 495°. *Ans. b,* 410 sec.

It is to be noted, however, that the rule as to the uniform effect of temperatures has been tested only for reactions which take place at a conveniently measurable rate, and that even among these there are a few striking exceptions; thus the rate of the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ has been found actually to decrease with rise of temperature.

15. Relation between the Effects of Temperature on Reaction-Rate and on Reaction Equilibrium. — The effect of temperature on the equilibrium-constant K is according to the laws of thermodynamics expressed by the van't Hoff equation (VII, 16), as follows:

$$\frac{d \ln K}{dT} = \frac{\Delta E}{R T^2}. \quad (13)$$

In this equation ΔE denotes the increase in energy-content attending a reaction $aA + bB + \dots = eE + fF + \dots$ whose equilib-

rium condition at T° is represented by a constant K equal to $(E)^c(F)^f \dots / (A)^a(B)^b \dots$, the equilibrium concentrations (E) , $(F) \dots$ being expressed as volume-molalities.*

The quantity ΔE is the difference in the energy-content E_s of the reaction-products and that E_l of the reactants. And it has been seen (VI, 5) that the equilibrium-constant K is the ratio of the specific reaction-rate k_l of the direct reaction to that k_s of the opposing reaction. Substitution of these quantities in the van't Hoff equation gives:

$$\frac{d \ln k_l}{dT} - \frac{d \ln k_s}{dT} = \frac{E_s}{R T^2} - \frac{E_l}{R T^2}. \quad (14)$$

It will be noted that this equation is the difference of two equations which contain quantities relating to the reactants or to the products, respectively. To make these equations general there must, however, be introduced into each of them a thermodynamically indeterminate quantity E_0 which has the same value for the direct and opposing reactions; for obviously the van't Hoff equation still results when the rate equations are so generalized. The equations then become:

$$\frac{d \ln k_l}{dT} = \frac{E_0 - E_l}{R T^2}; \quad \frac{d \ln k_s}{dT} = \frac{E_0 - E_s}{R T^2}. \quad (15)$$

It is further evident that, to make Eqs. 15 identical with the experimentally established Arrhenius equation (Eq. 12), one must regard the quantities $(E_0 - E_l)/R$ and $(E_0 - E_s)/R$ as identical with the empirical quantities A_l and A_s in the Arrhenius equations for the direct and opposing reactions. It is also evident that one may consider the former quantities to be substantially independent of the temperature, since A_l and A_s are commonly found to vary only slightly with the temperature in the case of reactions taking place at a measurable rate.

These considerations indicate that the constant A multiplied by the gas-constant R is the difference of two energy quantities of which one (E_l or E_s) is the average energy-content

* For cases in which the equilibrium constant K is evaluated in terms of weight molalities, or partial-pressures, the van't Hoff equation becomes

$$\frac{d \ln K}{dT} = \frac{\Delta H}{R T^2}.$$

of the molecules in their ordinary state and the other (E_0) is a larger quantity determined, almost independently of the temperature, by the reaction which they undergo. This conclusion may be expressed by writing the Arrhenius reaction-rate equations in the following form, it being understood that E_0 and E'_1 or E'_2 are quantities that vary only slightly with temperature.

$$\frac{d \ln k_1}{dT} = \frac{E_0 - E_1}{R T^2} = \frac{E'_1}{R T^2}; \quad \frac{d \ln k_2}{dT} = \frac{E_0 - E_2}{R T^2} = \frac{E'_2}{R T^2}. \quad (16)$$

Theoretical interpretations of the energy quantities E_0 and E' are considered in the following articles.

16. Energy Interpretation of the Effect of Temperature on Reaction-Rate. — The occurrence in Eqs. 16 of two energy quantities E_1 or E_2 and E_0 (one of which is equal to the average energy-content of the molecules at the specified temperature T , and the other of which is determined, independently of the temperature, by the reaction which they undergo) suggests the following explanation of the mechanism of reaction-rate in general. In order that (in the case of a multimolecular reaction) two or more molecules may be *reactive* (that is, be capable of reacting with one another when they collide) they must together possess at least a certain critical energy-content E_0 (which in the case of reaction-rates slow enough to be measured is much greater than the normal or average energy-content E_1 of these molecules). In other words, the molecules that are at any moment reactive (which in slow reactions constitute a small fraction of all the molecules) must in some way have had their energy-content increased from E_1 to E_0 , that is, by an amount $E_0 - E_1$. This increment, commonly called the *energy of activation* E'_1 , may evidently be experimentally determined by measuring the change of the specific reaction-rate with the temperature and applying the Arrhenius equation to the results. The fact that the same energy-value E_0 occurs in the reaction-rate equations (Eq. 16) for the direct and opposing reactions further indicates that the molecules involved in these respective reactions, to become reactive, must attain (whatever the temperature) the same minimum critical energy E_0 .

These relations will be made clearer by the following specific example. Consider that at any temperature the

bimolecular reaction $2\text{HI} = \text{H}_2 + \text{I}_2$ may take place when and only when two colliding HI molecules together possess a sum-total of energy greater than a certain critical value E_0 , which largely exceeds (at temperatures where the reaction is slow) the average energy E_i of two HI molecules in the ordinary state. Consider also that the reverse reaction $\text{H}_2 + \text{I}_2 = 2\text{HI}$ may take place when and only when an H_2 and an I_2 molecule collide which together possess a sum-total of energy greater than this same critical value E_0 , which largely exceeds the average sum-total of energy E_s of one H_2 and one I_2 molecule in the ordinary state. Then the ordinary reaction, by which two "average" molecules of HI are converted into "average" molecules of H_2 and I_2 , may be considered (for the case that the reactive molecules do not attain *more* than the minimum critical energy) to take place in three steps, as follows:

(1) Conversion of two average HI molecules with total energy-content E_i into two reactive or activated molecules HI' with total energy-content E_0 , hence with absorption of the energy $E_0 - E_i$, the energy of activation E'_i of two average HI molecules.

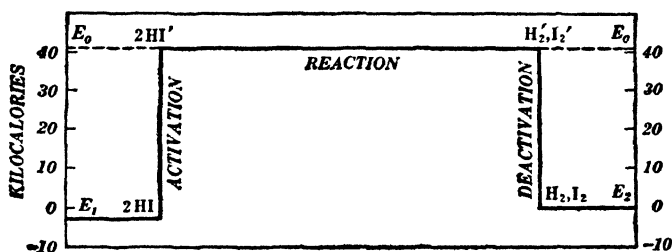
(2) Conversion of these activated HI' molecules into reactive or activated H'_2 and I'_2 molecules, without change of energy-content.

(3) Conversion of the activated H'_2 and I'_2 molecules into average H_2 and I_2 molecules, with energy-content E_s , hence with evolution of the energy $E_0 - E_s$, equal and opposite in sign to the energy of activation E'_s of an average H_2 and an average I_2 molecule.

This is illustrated by Fig. 1. In this figure the abscissas do not have quantitative significance, but represent the successive states of the system. The ordinates represent the energy-content at 400°C , expressed in kilocalories (kcal.) and referred as usual to the energy-content of the elementary gaseous substances H_2 and I_2 as zero. The energy-content (-3.1 kcal.) of 2HI (in the ordinary state at 400°C) is put equal to its energy of formation (from H_2 and I_2 at 400°C) as determined by heat measurements. The energy-content (40.9 kcal.) of $2\text{HI}'$ or of $\text{H}'_2 + \text{I}'_2$ (in the activated state) is shown larger than this by the

energy of activation (44.0 kcal.) of 2HI that is computed from the observed temperature-coefficient of its rate of decomposition. The energy of deactivation of $H_2 + I_2$ that is shown in the figure is this same value (-40.9 kcal.). It should be equal but opposite in sign to the energy of activation of $H_2 + I_2$ computed from the temperature-coefficient of their rate of combination. This computed value is 40.0 kcal., in satisfactory agreement with the energy of deactivation (-40.9 kcal.) found by difference.

FIGURE 1. ENERGY RELATIONS IN THE DECOMPOSITION OF HYDROGEN IODIDE.



The energies of activation, calculated by Eq. 16 from the temperature-coefficients of the reaction-rates, have been found to have the following values for certain reactions (*Hinshelwood, 1929*). For comparison the calorimetrically determined energy-increases attending the various reactions are shown in the last column of the table. (These last values refer to the reaction-temperature (400°C) in case of the first two reactions, but to room temperature in the case of the other reactions.)

TABLE V. ENERGIES OF ACTIVATION OF REACTANTS.

Reaction	Temperature	Energy of Activation E'	Energy-Increase $E_2 - E_1$ for the Reaction
$2\text{HI} = \text{H}_2 + \text{I}_2$	400°C	44,000 cal.	+ 3,100 cal.
$\text{H}_2 + \text{I}_2 = 2\text{HI}$	400	40,000	- 3,100
$\text{N}_2\text{O} = \text{N}_2 + \frac{1}{2}\text{O}_2$	665	53,000	- 17,000
$2\text{NO}_2 = 2\text{NO} + \text{O}_2$	302	32,000	28,000
$2\text{Cl}_2\text{O} = 2\text{Cl}_2 + \text{O}_2$	111	21,000	- 37,140
$\text{N}_2\text{O}_5 = \text{NO} + \text{NO}_2 + \text{O}_2$	32	24,700	—
$\text{CH}_3\cdot\text{N}:\text{N}\cdot\text{CH}_3 = \text{N}_2 + \text{C}_2\text{H}_6$	303	51,200	—

17. Molecular Interpretation of the Effect of Temperature on Reaction-Rate. — The most obvious process by which molecules may attain the required energy of activation is through collisions with other molecules; for Maxwell's distribution law (*III*, 19) shows that collisions cause some of the molecules to have at any moment kinetic energies much larger than the average value. Moreover, the law shows (Eq. 36; *III*, 19) that the fraction n_0/n of the molecules with translational kinetic energies exceeding some definite value E_0 which is large in comparison with the average value increases very rapidly with the temperature. Thus, calculation shows (Table V; *III*, 19) that the fraction of the molecules with kinetic energies exceeding a value twenty times the mean value at 0° increases 2.82 fold between 0° and 10° . This large increase with the temperature of molecules with high kinetic energies is especially striking when it is considered that for this same temperature increase their mean kinetic energy increases only 1.037 fold. Since quantitative applications of the Maxwell equations are rather complicated, the kinetic theory of reaction-rate will not be further considered here.



CHAPTER VII

THE EQUILIBRIUM OF CHEMICAL CHANGES

I. GENERAL CONSIDERATIONS.

1. General Considerations. — The mass-action law of chemical equilibrium as commonly stated (Eqs. 91a, 92; *IV*, 45) has been shown (*VI*, 5) to follow directly from the mass-action law of reaction-rate, and also (*IV*, 46) from the second law of thermodynamics. In the thermodynamic derivation it was made evident that the law is exact only in the case of reactions between perfect gases and perfect solutes; but that it holds approximately in the case of gases at moderate pressures, of electrically neutral solutes at moderate concentrations, and of ions at small concentrations.

There has also been already presented a thermodynamic derivation of the mass-action law in forms (Eqs. 93(a, b), 94; *IV*, 45) which are independent of the laws of perfect gases or of perfect solutions. This derivation involved the concept of an intensive property of any molecular species called its activity, which was defined (Eq. 83; *IV*, 43) in terms of its molar free energy. The derivation also involved the definition of certain standard states (*IV*, 44) of any such species to which its activity may be referred. These standard states were chosen so as to make the resulting exact expression for the mass-action law identical in form with the more commonly used approximate expression — the partial pressures of gaseous molecular species, and the molal-concentrations (or mol-fractions) of dissolved molecular species in the approximate expression being replaced in the exact expression by the corresponding relative activities (called fugacities in the case of the gaseous species). However, in order to apply the mass-action law in its exact form, it was shown necessary to determine for each molecular species involved in the equilibrium its so-called activity-coefficient (*IV*, 44), an empirical factor by which the partial pressure of a gaseous species (as calculated by Dalton's law), or the molal concentration (or mol-fraction) of a dissolved species, in the equilibrium

mixture must be multiplied to obtain the corresponding fugacity, or activity. A few of the experimental methods (*IV*, 44; *V*, 29, 33) by which such correction factors can be obtained have likewise been considered. Values for ion-activity-coefficients at 25° obtained by a greater variety of methods are recorded in Table III (*VII*, 6).

In this chapter are considered applications of the mass-action law to reactions taking place in both homogeneous and heterogeneous systems — that is to say, to reactions between gases in gaseous mixtures, or between solutes in some solvent, and to reactions between solid (or liquid) substances and substances present in a second (liquid or gaseous) phase. In considering liquid solutions the applications are limited to metathetical reactions between electrolytes in aqueous solution, not only on account of the chemical importance of such reactions, but because such reactions take place rapidly (*VI*, 10) and reach a state of equilibrium in a short period of time. There is also considered the effect of temperature on chemical equilibrium.

In solving mass-action problems, the laws of perfect gases and perfect solutions will in general be assumed; but deviations from such laws will often be taken into consideration by using the exact form of the mass-action equation and the results calculated by the two procedures then compared.

II. THE MASS-ACTION LAW FOR REACTIONS
BETWEEN GASES.

2. Gaseous Dissociation. — A chemical change which consists in the splitting of a substance with complex molecules into one or more substances with simpler molecules is called dissociation. Thus, the reactions $I_2 = 2I$, $NH_4Cl = NH_3 + HCl$, and $2CO_2 = 2CO + O_2$, are examples of dissociation. The fractional extent to which the dissociating substance has been decomposed is called its degree of dissociation, or simply its *dissociation* (γ). The equilibrium-constant of such a reaction is commonly called the *dissociation-constant* of the dissociating substance.

It is characteristic of such reactions that the number of molecules increases when the dissociation increases. Since the pressure-volume product of gases increases correspondingly, the degree of dissociation can always be determined by measuring the volume or density of the gas at a known temperature and pressure, and comparing it with that calculated for the undissociated or completely dissociated substance, as is illustrated by Probs. 15, 16 (*III*, 8), and by Prob. 2 below.

Another common method of determining the composition of the equilibrium mixture is to cool it suddenly to a lower temperature at which the reaction-rate is so small that the original equilibrium is not displaced, and then to analyze the mixture. This method presupposes that there is no change in the composition during the short period of cooling. This condition may be practically realized in cases where the rate at which the equilibrium is established is comparatively slow even at the higher temperature, or in cases where the reaction takes place only in contact with a catalyst. In the latter cases the equilibrium-mixture can be separated from the catalyst, and subsequently cooled without the danger of any change taking place.

*Applications of the Mass-Action Law to
Gaseous Dissociation.*

- Prob. 1.* — *a.* Formulate the mass-action expression for the dissociation of sulfur trioxide into sulfur dioxide and oxygen.
b. At 630° and 1 atm. the sulfur trioxide is just one third dis-

sociated. Calculate the dissociation-constant of sulfur trioxide in terms of pressure.

Prob. 2. — Show how the dissociation (γ) of sulfur trioxide could be calculated from measurements of the density (d) of the equilibrium mixture at the temperature (T) and pressure (p).

Prob. 3. — A mixture consisting of 1 mol of SO_2 and 1 mol of O_2 is passed at 630° and 1 atm. through a tube containing finely divided platinum so slowly that equilibrium is attained, and the issuing gas is cooled and analyzed by absorbing the sulfur dioxide and trioxide by potassium hydroxide and measuring the residual oxygen gas. At 0° and 1 atm. the volume of this residual gas was found to be 13,780 ccm., corresponding to 0.615 mol. *a.* Calculate the dissociation-constant of sulfur trioxide. *b.* Calculate the ratio of the mols of sulfur trioxide to the mols of sulfur dioxide in an equilibrium mixture at 630° in which the partial pressure of oxygen is 0.25 atm.

Prob. 4. — At a certain temperature a definite quantity of phosphorus pentachloride gas has at 1 atm. a volume of 1 liter, and under these conditions it is about 50% dissociated into PCl_3 and Cl_2 . Show by reference to the mass-action expression whether the dissociation will be increased or decreased: *a.* when the pressure on the gas is reduced till the volume becomes 2 l.; *b.* when nitrogen is mixed with the gas till the volume becomes 2 l., the pressure being still 1 atm.; *c.* when nitrogen is mixed with the gas till the pressure becomes 2 atm., the volume being still 1 l.; *d.* when chlorine is mixed with the gas till the pressure becomes 2 atm., the volume being still 1 l.; *e.* when chlorine is mixed with the gas till the volume becomes 2 l., the pressure being still 1 atm. — In answering these questions consider whether the first effect of the change in conditions (assuming that no reaction takes place) is to increase or decrease the value of the ratio $p_{\text{Cl}_2} p_{\text{PCl}_3} / p_{\text{PCl}_5}$, and in which direction the reaction must take place in order to restore the equilibrium-value of this ratio.

Prob. 5. — *a.* Derive for the dissociation of water-vapor into hydrogen and oxygen a mass-action expression which will show how the dissociation γ varies with the total pressure p . *b.* At 2000° the dissociation is 2.0% when the total pressure is 1 atm. Calculate the dissociation when the total pressure is 0.33 atm. (as it is approximately in the gaseous mixture produced by burning hydrogen with the minimum amount of air). Solve the equation approximately, neglecting the (small) value of the dissociation where this is justifiable. *Ans. b, 2.9%.*

3. Metathetical Gas Reactions. — Examples of metathetical gas reactions whose equilibrium has been investigated

are:



An important principle in regard to them, illustrated by Prob. 7 below, is that the equilibrium-constant of any metathetical gas reaction can be calculated from the dissociation-constants of the compounds involved in it.

Another important principle relates to the effect of pressure. It states that increase of pressure causes the equilibrium of any gaseous reaction to be displaced in that direction in which the number of molecules, and therefore the volume of the gas, decreases. This principle has already been illustrated by the fact that dissociation is decreased by increase of pressure. It is demonstrated in Prob. 8.

Prob. 6. — Combustion of "Water-Gas" with Insufficient Oxygen. — The equilibrium-constant of the reaction $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ at 1120° is 2.0. Calculate the ratio of the mols of CO_2 to the mols of H_2O that are formed when a "water-gas" consisting of 1 mol of CO and 1 mol of H_2 is burnt at 1120° with $\frac{1}{2}$ mol of O_2 . Assume that equilibrium is attained and that the quantity of the oxygen which remains uncombined is negligible.

Prob. 7. — Metathetical Equilibrium-Constants in Relation to Dissociation-Constants. — The equilibrium-constant of the reaction $2\text{CO}_2 = 2\text{CO} + \text{O}_2$ at 1120° is 1.4×10^{-12} . *a.* Calculate the partial pressure of the oxygen in the equilibrium mixture of Prob. 6. *b.* Calculate the dissociation-constant of water-vapor at 1120° . *c.* Show what relation exists between the dissociation-constants K_W and K_{CO_2} of water-vapor and of carbon dioxide and the equilibrium-constant K of the reaction $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$. *Ans. b.* 3.5×10^{-13} atm.

Prob. 8. — Effect of Pressure on Gaseous Equilibrium. — Prove that the equilibrium of any chemical reaction $aA + bB = cC + dD$, must be displaced in the direction in which the number of molecules decreases when the total pressure p of the equilibrium mixture (in which the substances are present at mol-fractions X_A , X_B , X_C , and X_D) is increased.

Prob. 9. — Production of Hydrogen from "Water-Gas." — A quantity of "water-gas" consisting of 1 mol of CO and 1 mol of H_2 is mixed with 5 mols of steam, and this mixture is passed slowly at 1 atm. and 500° over a suitable catalyst, whereby the reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ takes place. The gases are then cooled in order to condense the steam. The equilibrium-constant of the

reaction at 500° is 5.5. *a.* Calculate the smallest mol-fraction of CO in the resulting gas mixture attainable by this process. *b.* Show whether this minimum percentage of CO could be diminished by passing the gas mixture over the catalyst at 5 atm. and 500° . *c.* Show whether it could be diminished by passing it over the catalyst at 1 atm. and 400° , noting the values of the equilibrium-constant already given at 1120° and 500° . *d.* State the effect of the lower temperature on the time required for reducing the percentage of CO to any definite value. *e.* In practice the above process may yield a mixture containing 4 mol-percent of CO, 65 mol-percent of H_2 , and 31 mol-percent of CO_2 . To free this mixture from CO_2 , it is passed at 30 atm. up a tower through which water at 17° is trickling. Calculate the minimum volume of water theoretically required to remove 99% of the CO_2 from 100 mols of the gas mixture. Assume Henry's Law to hold true, and take the solubility of CO_2 in water at 17° and 1 atm. as 0.0425 molal. *f.* Calculate the percentage of the hydrogen that is lost by dissolving in the water, from the fact that the solubility of hydrogen gas in water at 17° and 1 atm. is 0.00084 molal. *Ans.* *e.* 77.7 liters.

III. THE MASS-ACTION LAW FOR REACTIONS BETWEEN SOLUTES.

4. Ionization of Slightly Ionized Univalent Acids and Bases. — The mass-action law has been found to be applicable to the ionization of slightly ionized monobasic acids and monacidic bases. This is illustrated by the following values at 18° of the ionization, taken equal to the conductance-viscosity-ratio, and of the *ionization-constant* K for ammonium hydroxide, that is, the equilibrium-constant of the reaction $\text{NH}_4\text{OH} = \text{NH}_4^+ + \text{OH}^-$.

IONIZATION OF AMMONIUM HYDROXIDE AT 18°

Formality	0.500	0.300	0.100	0.010	0.001
Ionization	0.0056	0.0074	0.0130	0.0405	0.123
$K \times 10^6$	15.8	16.6	17.1	17.1	17.1

The ionization-constant varies greatly with the composition and structure of the acid or base, as will be seen from the following values.

TABLE I. IONIZATION-CONSTANTS OF ACIDS AND BASES AT 25°.

<i>Acid</i>	$10^6 K$	<i>Acid</i>	$10^6 K$	<i>Acid</i>	<i>Values of $10^6 K$</i>		
HCN	0.0007	HCO ₂ H	177	C ₆ H ₅ CO ₂ H	60	60	60
HBO ₂	0.0007	CH ₃ CO ₂ H	18		<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
HCIO	0.03	C ₂ H ₅ CO ₂ H	13	C ₆ H ₄ OHCO ₂ H	1000	85	28
HNO ₂	450	<i>n</i> -C ₃ H ₇ CO ₂ H	15	C ₆ H ₄ ClCO ₂ H	1280	152	91
HF	750	CH ₂ ClCO ₂ H	1378	C ₆ H ₄ NO ₂ CO ₂ H	6400	338	388

<i>Base</i>	$10^6 K$
NH ₄ OH	18
CH ₃ NH ₂ OH	440
C ₆ H ₅ NH ₂ OH	0.0004

Derivation of Ionization-Constants from Conductance Data.

Prob. 10. — *a.* Calculate the ionization constant of acetic acid at 25° corresponding to each of the following equivalent conductance values (*MacInnes and Shedlovsky, 1932*):

Conc. c vf.	0.200	0.100	0.050	0.00984	0.00103	0.0000
Conduct. Λ_c	3.650	5.200	7.356	16.367	48.133	390.59
Ratio $\Lambda_c/350.59$	0.0093	0.0133	0.0188	0.0419	0.123	1.0000

b. With the aid of the constant thus obtained calculate the ionization of the acid and its equivalent conductance in 1.0 normal solution. *c.* Formulate a general expression for the change in the ionization γ with the concentration c of the acid.

Prob. 11. — *a.* State what two assumptions, inexact because of ion-attraction, are involved in the calculation of the ionization-constant in Prob. 10. *b.* By reference to the ionic strengths involved, explain why the ionization-constants so calculated are substantially identical with the true ionization-constant expressed in terms of activity. Note that when corrections for ion-attraction are applied to the above data, the ionization-constant is found to be 1.753×10^{-5} .

Prob. 12. — *Effect of the Presence of a Substance with a Common Ion.* — *a.* Show that the hydrogen-ion concentration of an acetic acid solution is decreased by the addition of sodium acetate approximately in the proportion in which the concentration of the acetate-ion is increased. *b.* Calculate the ionization of acetic acid and the corresponding hydrogen-ion concentration in a solution 0.1 formal both in acetic acid and in sodium acetate at 25° , assuming the ions to behave as perfect solutes. *c.* Repeat the calculations with the aid of Eq. 47 (V , ?) for the activity-coefficient α at 25° of an ion in a solution of ionic strength μ . *d.* What is the pH of the solution?

5. Ionization of Salts, Strong Acids, and Strong Bases. —

When the ionization of salts, strong acids, and strong bases is determined from the equivalent conductances by assuming constant ion-mobilities, or from freezing-points by assuming the law of perfect solutes, the ionization values so obtained do not decrease with increasing concentrations as the mass-action law requires. Namely, in the case of the conductance, its fractional decrease $(\Lambda_0 - \Lambda)/\Lambda_0$ was found experimentally to be proportional to the square-root of the concentration so long as this is small (V , 21) whereas for a diionic salt the mass-action law $\gamma^2 c = K(1 - \gamma)$ requires that the decrease $1 - \gamma$ in the ionization γ of a largely ionized substance be at first nearly proportional to the concentration c , since $1 - \gamma = (1/K)c$ approximately so long as γ^2 has not changed greatly from its initial value unity. How great the divergence is from the requirements of the mass-action law is shown by Table II, which contains the

values for potassium chloride at 18° of the conductance-ratio and of the ionization γ that would be calculated by the above mass-action expression from the ionization-constant K at 0.1 normal under the arbitrary assumption that at this concentration the conductance-ratio is equal to the ionization. The table contains also the corresponding values of the ionization-constant K computed under this assumption.

TABLE II. THE CONDUCTANCE-RATIO IN RELATION TO THE MASS-ACTION LAW.

Formality	0.001	0.01	0.05	0.10	0.20	0.50
Conductance-ratio	0.982	0.94	0.89	0.86	0.83	0.79
γ from Mass-action	0.998	0.98	0.92	0.86	0.78	0.63
Ionization-constant K	0.053	0.15	0.36	0.53	0.81	1.49

The ionization values calculated from the freezing-point under the assumption that the ions are perfect solutes are not greatly different from those corresponding to the conductance-ratio, and they show an entirely parallel divergence from the requirements of the mass-action law.

This striking discordance with the mass-action law might, to be sure, be explained in the case of the conductance-ratio, and also in the case of the freezing-point, without assuming complete ionization, by recognizing that the ions are imperfect solutes, and in the case of conductance, retaining the hypothesis of constant ion-mobility. But consideration of all the experimental facts, as well as of the ion-attraction theory (*V*, 27), seems to justify the simpler hypothesis of complete ionization, as shown in *V*, 24. This hypothesis, combined with the conclusion that ions are imperfect solutes, is therefore now generally adopted. Accordingly, in the following articles complete ionization will be assumed; but for the sake of simplicity, no correction will be made for the abnormal mass-action of the ions, unless, for comparison, the exact treatment is also called for. Values for the activity-coefficients of ions needed for such exact treatment are considered in the next article.

6. Values of Activity-Coefficients of Ions. — The two methods previously described for the direct determination of the mean activity-coefficients of the ions of salts, strong acids and bases — namely from vapor-pressure (*IV*, 44), or electromotive

force (*V*, 29, 33) measurements — are applicable only in the case of volatile solutes or of solutes which can be transferred electrically from one solution to another.

A more general method is based on Eq. 81 (*IV*, 42), which gives a thermodynamic relation between the molar free energy of the solvent and that of the solute. The method consists in measuring the (solvent) vapor-pressures at any definite temperature, or the freezing-points of solutions of the salt (strong acid or base) at a series of concentrations extending to very dilute solutions. Relative values of the molar free energy and the activity of the solvent in such solutions are readily computed from such measurements, as illustrated by Probs. 66 and 67 (*IV*, 44); and the corresponding relative values for the formular free energy of the dissolved salt (strong acid or base) may then be computed from them with the aid of Eq. 81. Finally from these relative values for the formular free energy of the (completely ionized) electrolyte may be calculated values for the mean activity-coefficient of its ions, as illustrated by Probs. 43, 44 (*V*, 29), and Prob. 52 (*V*, 33).

Precise methods have been devised for measuring directly the freezing-point lowering produced by the added solute, and are extensively used to determine the mean ion-activity-coefficient of strong electrolytes, especially in very dilute solutions. Although such a freezing-point method has the disadvantage of giving the molar free energy of the solvent at the freezing-point of the solution, the variation of this quantity with the temperature may be calculated from observed heats of dilution of the electrolyte with the aid of thermodynamic relations which need not here be considered.

The effect of concentration on the mean ion-activity-coefficient at 25° of various types of strong electrolytes is illustrated by Table III (*Landolt-Börnstein*, *Ib*, 1114 (1931); *IIIc*, 2141 (1936)). The observed values are based on precise freezing-point and electromotive-force measurements. In the rows designated "limiting law" and "theory" are recorded for comparison values of the activity-coefficients of the separate ions as calculated by the dilute solution ion-attraction Eqs. 45 and 47 (*V*, 7). These equations are:

$$\log \alpha_{\pm} = -0.505 z_{\pm}^2 \sqrt{\mu}; \quad \text{and} \quad \log \alpha_{\pm} = -0.505 z_{\pm}^2 \sqrt{\mu} / (1 + \sqrt{\mu}).$$

Prob. 13. — Mean Ion-Activity-Coefficients from Ion-Attraction Theory. — *a.* Calculate the activity-coefficient of the K^+ -ion and that of the SO_4^{2-} -ion in 0.1 wf. K_2SO_4 at 25° with the aid of Eq. 47 (V, 7). *b.* From these values compute the corresponding mean ion-activity-coefficient of K_2SO_4 . *c.* Formulate a general expression for the mean ion-activity-coefficient of any univalent salt at 25° and weight-formality c .

The adequacy of the second of the above ion-attraction equations for computing the activity-coefficients of ions in solutions of ionic strength less than 0.1 is shown by the agreement of the "observed" values of the mean ion-activity-coefficients with the "theory" values in Table III. An even closer agree-

TABLE III. MEAN ACTIVITY COEFFICIENTS OF THE IONS AT 25° .

Weight-Formality	0.005	0.01	0.02	0.05	0.10	0.20	0.50	1.00	3.00
<i>Limiting Law for A^+E^-</i>	0.921	0.890	0.848	0.771	0.692	0.595	0.430	0.313	0.133
<i>Theory for A^+E^-</i>	0.926	0.900	0.866	0.809	0.756	0.698	0.618	0.559	0.478
<i>Observed for HCl</i>	0.928	0.904	0.874	0.830	0.795	0.766	0.757	0.810	1.320
NaCl	0.928	0.904	0.876	0.829	0.789	0.742	0.683	0.659	0.709
KCl	0.926	0.899	0.866	0.815	0.764	0.712	0.644	0.597	0.571
KOH	0.927	0.901	0.868	0.810	0.759	0.710	0.671	0.679	0.903
KNO ₃	0.927	0.899	0.863	0.794	0.724	0.653	0.543	0.449	—
AgNO ₃ *	0.925	0.896	0.858	0.787	0.717	0.633	0.501	0.390	—
KIO ₃ , NaIO ₃	0.924	0.895	0.856	0.784	0.714	—	—	—	—
<i>Theory for $A^{++}E^-$</i>	0.562	0.460	0.359	0.238	0.165	0.101	0.066	0.045	—
<i>Observed for MgSO₄</i>	0.572	0.471	0.378	0.262	0.195	0.142	0.091	0.067	—
CuSO ₄	0.560	0.444	0.343	0.230	0.164	0.108	0.066	0.044	—
<i>Theory for $A_2^+E^-$ or $A^{++}E_2^-$</i>	0.776	0.710	0.634	0.523	0.439	0.362	0.274	0.229	—
<i>Observed for BaCl₂</i>	0.781	0.725	0.659	0.556	0.496	0.440	0.396	0.399	—
Pb(NO ₃) ₂ *	0.763	0.687	0.596	0.464	0.373	0.275	0.168	0.112	—
K ₂ SO ₄	0.781	0.715	0.642	0.529	0.441	0.361	0.262	0.210	—

* Values at 0° .

ment is obtained when for each electrolyte the individual ion-activity-coefficients at 25° are calculated by Eq. 46 (V, 7),

$$\log \alpha_A = -0.505 z_A^2 \sqrt{\mu} / (1 + D_A \sqrt{\mu}),$$

in which D_A is an empirical constant characteristic of the ion A and involving its apparent diameter, or the average distance of nearest approach to other ions in the solution. The observed

values of the mean ion-activity-coefficients thus confirm the statement previously made (V, 7) that the average value of D_A at 25° for a large number of ions is approximately equal to unity.

Even in solutions of higher ionic strength the assumption is often made that the activity-coefficient of any ion species A at a definite temperature is determined solely by the ionic-strength of the solution, regardless of the nature of the ions which contribute to this ionic-strength. This assumption, though useful as an approximation, is incorrect, and a more rigorous treatment of the ion-attraction theory brings out the fact that the activity-coefficient of the ion A is affected to some extent by each of the other ion species, and also by molecular species which are electrically neutral. A comparison of the "observed" and "theory" values of the mean ion-activity-coefficients in Table III indicates, however, that such specific effects in solutions of ionic-strength less than 1.0 are as a rule not very large, and hence that only a correspondingly small error is introduced when they are neglected in calculating the activity-coefficients of the individual ions.

7. The Ionization of Water. — The dissociation of water into H^+ and OH^- ions is extremely small, as is shown by the very small conductance of the purest water that has been prepared. This ionization is, nevertheless, of great significance from an equilibrium viewpoint, since water is involved in many ionic reactions, for example, in the hydrolysis of salts considered in the next article.

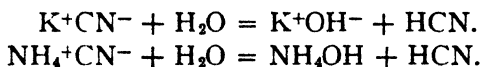
The complete expression for the equilibrium-constant of the reaction $H_2O = H^+ + OH^-$, commonly called the *ionization-constant* K_w of water, would contain a term representing the activity $[H_2O]$ of the chemical species H_2O . This activity of water in the solution is usually referred to the activity of pure water as unity (IV, 44), and is thereby made equal to the ratio p/p_0 of its vapor-pressure in the solution to that of pure water. Now, since this ratio in a solution of solute content even as high as 1 weight-molal differs according to Raoult's law from unity by only 1.8 percent, the ionization-constant may in aqueous solutions of moderate concentration be written in the simple form: $K_w = [H^+][OH^-]$, or for perfect solutions $K_w = (H^+)(OH^-)$.

The ionization-constant of water has been determined by a number of different methods including that based on the conductance of carefully purified water, illustrated by Prob. 30 (V, 25). Its value has been found to be 0.11×10^{-14} at 0° ; 0.58 at 18° ; 1.00×10^{-14} at 25° ; and 48×10^{-14} at 100° .

From the value of this ionization-constant there can be calculated the concentration of hydrogen-ion in any dilute aqueous solution of known hydroxide-ion concentration, and conversely.

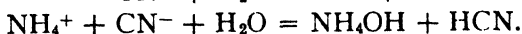
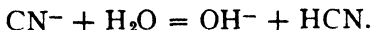
Prob. 14. — Concentration of Hydrogen-Ion in Aqueous Solutions. — Calculate the concentration of hydrogen-ion at 25° , *a*, in pure water; *b*, in 0.1 wf. NaOH solution, assuming the ions to behave as perfect solutes. *c*. Calculate the activity and the concentration of hydrogen-ion in 0.1 wf. NaOH, using the theoretical value (given in Table III) of the activity-coefficient of the ions.

8. The Hydrolysis of Salts. — When either the acid or base of a salt has a very small ionization-constant, the salt in aqueous solution reacts with the water to an appreciable extent with formation of the acid and base. This phenomenon is called hydrolysis; and the fraction of the salt hydrolyzed is called the degree of hydrolysis, or simply the *hydrolysis (h)*. Thus, at 25° in 0.01 formal solution potassium cyanide and ammonium cyanide are hydrolyzed to the extent of 3.7 percent and 45.0 percent, respectively, according to the reactions,



As is done in the preceding chemical equations, it is convenient to indicate largely ionized substances, whose ionization though unknown is considered to be complete even at high concentrations, by attaching + and - signs to their ions, and to indicate slightly ionized substances, whose ionization conforms to the mass-action law, by omitting these signs. The corresponding ion-reactions, the equilibrium conditions of which determine the extent of chemical change, are then readily written by omitting the ions common to the two sides of the chemical equation. Thus, the above hydrolysis equations written as ion-

reactions become:



It may be here noted that part of the ammonium hydroxide produced by the hydrolysis of ammonium cyanide is converted into ammonia and water by the reaction $\text{NH}_4\text{OH} = \text{NH}_3 + \text{H}_2\text{O}$, and that as a consequence the equilibrium of the reaction $\text{NH}_4^+ + \text{CN}^- + \text{H}_2\text{O} = \text{NH}_4\text{OH} + \text{HCN}$ is displaced in the direction of increased hydrolysis. Now it follows from application of the mass-action law to the reaction $\text{NH}_4\text{OH} = \text{NH}_3 + \text{H}_2\text{O}$ that the relative proportions of NH_4OH and NH_3 produced by hydrolysis are substantially independent of the salt concentration, since, for the reasons presented in the preceding article, the activity of the water in such solutions remains nearly constant, and is by definition of its standard state as solvent equal to unity. The concentration ratio $(\text{NH}_3)/(\text{NH}_4\text{OH})$ cannot, however, be determined by experiment. It is for this reason that Henry's law is expressed for ammonia in the form $K_c = [(\text{NH}_3) + (\text{NH}_4\text{OH})]/p_{\text{NH}_3}$, and the standard states of unit-activity of both chemical species, NH_3 and NH_4OH , are correspondingly so defined (Prob. 68; IV, 44) that in solutions of moderate solute concentration the activity of NH_3 is made equal to that of NH_4OH , and each is made equal to the sum of the weight-molalities as expressed by the equation $[\text{NH}_3] = [\text{NH}_4\text{OH}] = (\text{NH}_3) + (\text{NH}_4\text{OH})$ for perfect solutions. By such definitions the equilibrium-constant of the reaction $\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4\text{OH}$ is arbitrarily made equal to unity at all temperatures; and also the equilibrium-constant of the reaction $\text{NH}_4^+ + \text{CN}^- = \text{NH}_3 + \text{HCN}$ is made identical in value with that of the reaction $\text{NH}_4^+ + \text{CN}^- + \text{H}_2\text{O} = \text{NH}_4\text{OH} + \text{HCN}$. Similar relations hold for the hydration of CO_2 (or other weak anhydrous acid or base), and for the hydrolysis of its salts.

The hydrolysis of salts can be experimentally determined by a variety of methods. It may be derived from measurements of the conductance of the salt, as in Prob. 31 (V, 25) and in Prob. 15 below; also from the effect of the salt on the rate of reactions whose rates are proportional to the concentration of hydroxide-ion or hydrogen-ion in the solution, as in Prob. 18

(VI, 8) and in Prob. 16 below. It may also be determined by measuring the distribution of the slightly ionized acid or base of the salt into an organic solvent, as in Prob. 17 below.

Prob. 15. — Determination of Hydrolysis by Conductance Measurements. — The specific conductance at 100° of a 0.025 formal solution of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (ammonium acetate) is 0.00685 reciprocal ohm; and that of a second solution 0.025 formal in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and 0.025 formal in NH_4OH is 0.00717 reciprocal ohm.

a. Neglecting the effect of ion-attraction on the ion-mobilities, calculate the hydrolysis of the ammonium acetate in the first solution, assuming that in the second solution the hydrolysis of the salt has been reduced to zero by the excess of base present and that the ionization and conductance of the base in the presence of its neutral salts are negligible. *b.* Show that the result is not seriously in error because the effect of ion-attraction was neglected. *Ans. a.* 4.5%.

Prob. 16. — Determination of Hydrolysis by Reaction-Rate Experiments. — The specific reaction-rate at 100° of the sugar hydrolysis has been found to be 0.0386 in a solution 0.001 formal in HCl , and to be 0.0946 in a solution 0.01 formal in AlCl_3 . Calculate the fraction of the salt that is hydrolyzed (into $\text{Al}(\text{OH})_3$ and 3HCl).

Prob. 17. — Determination of Hydrolysis by Distribution Experiments. — A 0.05 volume-formal solution of $\text{Na}_2\text{NH}_4\text{PO}_4$ in water is found to be in equilibrium with a 0.00173 volume-formal solution of NH_3 in chloroform at 18°. Calculate the hydrolysis of the salt into NH_4OH and $\text{Na}_2^{+}\text{HPO}_4^{-}$. The distribution-ratio for NH_3 between water and chloroform at 18° is 27.5.

The equilibrium-constant of a hydrolytic reaction is called the *hydrolysis-constant* K_h of the salt. Thus the hydrolysis-constants of potassium cyanide and ammonium cyanide are expressed by the equations:

$$K_h = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]};$$

and

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^{+}][\text{CN}^-]} = \frac{[\text{NH}_3][\text{HCN}]}{[\text{NH}_4^{+}][\text{CN}^-]}.$$

The activity of the water is not indicated in these equations since, as just stated, it is in moderately dilute solutions nearly equal to unity. The electrically neutral chemical species, HCN , NH_4OH , and NH_3 , may with slight error be assumed to behave as perfect solutes. The electrically charged ion-species, OH^- ,

CN^- , and NH_4^+ , show marked deviations from the laws of perfect solutes even in solutions of low ionic strength, and hence, for exact mass-action formulation, their activities should be computed from their weight-molalities and activity-coefficients as shown by the equations: $[\text{CN}^-] = \alpha_{\text{CN}}(\text{CN}^-)$; $[\text{OH}^-] = \alpha_{\text{OH}}(\text{OH}^-)$; and $[\text{NH}_4^+] = \alpha_{\text{NH}_4}(\text{NH}_4^+)$. Frequently, however, equilibrium concentrations calculated under the assumption that ions behave as perfect solutes are, due to compensation of errors, substantially equal to those calculated by the exact treatment. Thus, in the expression of the hydrolysis-constant of potassium cyanide, the ratio $[\text{OH}^-]/[\text{CN}^-]$ is substantially equal to the ratio $(\text{OH}^-)/(\text{CN}^-)$, since the ion-activity-coefficients, α_{OH} and α_{CN} , are nearly equal in value. It will be seen, however, that such a compensation does not take place in the hydrolysis-constant of ammonium cyanide; but even in this case, it is approximately true that from the hydrolysis of ammonium cyanide at one concentration its hydrolysis at a second concentration may be calculated under the assumption that the ion-activity-coefficients in conformity with the laws of perfect solutes are equal to unity. This follows from the fact that the mean ion-activity-coefficient of the salt, though considerably less than unity, does not vary rapidly with the salt concentration.

Just as the equilibrium-constant of a metathetical gas reaction is determined by the dissociation-constants of the compounds present (VII, 3), so the equilibrium-constant for any reaction between ionized substances in solution is determined by the ionization-constants of the partially ionized substances involved. Accordingly, the hydrolysis-constant of a salt is determined (as shown in Prob. 19) by the ionization-constant K_w of water and the ionization-constants K_a and K_b of the slightly ionized acid and base produced. The hydrolysis of salts can therefore be calculated from these ionization-constants (as in Prob. 20); and conversely, these ionization-constants can be derived from experimentally determined values of the hydrolysis (as in Prob. 21).

Prob. 18. — The Hydrolysis-Constant in Relation to the Hydrolysis. — a. Assuming the laws of perfect solutes, calculate

the value of the hydrolysis-constant at 25° for KCN, and that for NH_4CN from the facts that the values of the hydrolysis of these salts at 0.01 wf. are 3.7% and 45.0% respectively. *b.* Formulate a general expression showing how the hydrolysis h of the salt varies with its concentration c in the case of KCN, and of NH_4CN . *c.* Calculate the hydrolysis of NH_4CN in a solution 0.01 wf. in NH_4CN and 0.01 wf. in NH_4OH at 25°. *d.* Repeat the calculations assuming the ions to deviate from perfect solutes in accordance with the theoretical ion-attraction equation, and using the answer to *c* for evaluating the ionic strength in that solution. *Ans. c.* 27%.

Prob. 19. — The Hydrolysis-Constant in Relation to the Ionization-Constants. — a. Calculate the values of the hydrolysis-constant at 25° for KCN and for NH_4CN from the ionization-constants involved. *b.* Formulate general expressions for the relation between the hydrolysis-constant K_h of salts, like KCN and NH_4CN , and the ionization-constants K_w , K_a , K_b .

Prob. 20. — Calculation of Hydrolysis from the Ionization-Constants. — a. Calculate the concentrations of NH_4OH , H^+ , and OH^- , in a 0.1 wf. NH_4Cl solution at 25° from the ionization-constants, assuming the ions to behave as perfect solutes. *b.* Calculate, under the same assumption, the hydrolysis of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in 0.025 wf. solution at 25° from the ionization-constants. *c.* Repeat the calculations taking into consideration the effect of ion-attraction. *d.* What is the *pH* of each of these solutions?

Prob. 21. — Calculation of the Ionization of Water from the Hydrolysis of Salts. — Calculate the ionization-constant of water K_w at 100° from the hydrolysis of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ as determined in Prob. 15 and from the ionization-constants of NH_4OH and $\text{HC}_2\text{H}_3\text{O}_2$ at 100°, which have been found by conductance measurements to be 1.4×10^{-6} and 1.1×10^{-5} , respectively. Determine the ion-activity-coefficients by the ion-attraction equation $\log \alpha_A = -0.607 z_A^2 \sqrt{\mu}/(1 + \sqrt{\mu})$, which is based on the assumption that the dielectric constant of water at 100° is 55.3.

9. Ionization of Dibasic Acids and Their Acid Salts. — Polybasic acids ionize in stages; thus, a dibasic acid H_2A ionizes according to the equations $\text{H}_2\text{A} = \text{H}^+ + \text{HA}^-$ and $\text{HA}^- = \text{H}^+ + \text{A}^-$. The equilibrium-constants K_1 and K_2 of these reactions are called the ionization-constants for the first hydrogen and for the second hydrogen, respectively.

The ionization-constant for the first hydrogen is commonly derived from the conductance-ratio (as in Prob. 10), since the ionization-constant of the second hydrogen is usually so much

smaller than the ion-concentrations resulting from the secondary ionization are negligible in comparison with those from the primary ionization (especially in view of the common-ion effect). The values of the secondary ionization-constants are derived by special methods illustrated in Probs. 23-25.

The values at 25° of the constants for some important acids are given in the following table.

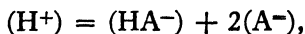
TABLE IV. IONIZATION-CONSTANTS OF POLYBASIC ACIDS AT 25°.

<i>Acid</i>	K_1	K_2	K_3	<i>Acid</i>	K_1	K_2
H ₂ SO ₄	Ionization complete	1.2×10^{-2}		H ₂ C ₂ O ₄ (Oxalic)	5.9×10^{-2}	6.4×10^{-5}
H ₂ SO ₃	1.2×10^{-2}	$5. \times 10^{-6}$		H ₂ C ₃ H ₄ O ₄ (Malonic)	1.4×10^{-3}	2×10^{-6}
H ₃ PO ₄	7.5×10^{-3}	6.2×10^{-8}	10^{-12}	H ₂ C ₄ H ₄ O ₄ (Succinic)	6.6×10^{-6}	3×10^{-8}
H ₂ CO ₃	4.5×10^{-7}	5.6×10^{-11}		H ₂ C ₄ H ₄ O ₆ (<i>d</i> = Tartaric)	9.7×10^{-4}	4×10^{-5}
H ₂ S	$9. \times 10^{-8}$	10^{-12}				
<i>Phthalic Acid</i> C ₆ H ₄ (CO ₂ H) ₂				<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
	K_1	1.3×10^{-3}		2.9×10^{-4}	3.1×10^{-4}	
	K_2	5.0×10^{-5}		2.5×10^{-5}	1.5×10^{-5}	

From the two ionization-constants of a dibasic acid and its formal concentration c the concentrations of the various substances H₂A, HA⁻, A⁼, and H⁺ present in its solution can be calculated. In solving such mass-action problems involving many substances, the best plan is to formulate first the equilibrium equations that must be satisfied — thus, in this case the equations $(H^+)(HA^-) = K_1(H_2A)$ and $(H^+)(A^-) = K_2(HA^-)$. For simplicity the ions are here assumed to behave as perfect solutes. The next step is to formulate the so-called condition equations, which sum up the concentrations of the separate forms in which an element or other constituent exists in the solution. Thus, in this case, for the total molal concentration $\Sigma(A)$ of the constituent A, and for that $\Sigma(H)$ of the hydrogen, we have:

$$\begin{aligned}(H_2A) + (HA^-) + (A^-) &= \Sigma(A) = c, \\ (H^+) + (HA^-) + 2(H_2A) &= \Sigma(H) = 2c.\end{aligned}$$

(It will be noted that one of these equations might be replaced by a simpler condition-equation of another kind; namely, by the equation,



which expresses the fact that positive and negative ions must be present in equivalent quantities.) We now have four independent equations containing four unknown concentrations. An exact algebraic solution of these equations is therefore possible. But, as such a solution is often very complicated, it is advisable to try first to simplify the condition-equations, which can often be done by neglecting in them the concentration of some substance which is small in comparison with the concentrations of each of the other substances occurring in the same equation. Thus, in this case the concentration (A^-) is small compared with the concentration (H_2A) because even the first hydrogen is split off to only a moderate extent, and it is small compared with the concentration (HA^-) for the reasons that K_2 is small in comparison with K_1 and that the hydrogen-ion produced by the ionization of the H_2A into H^+ and HA^- further decreases by the common-ion effect the ionization of the HA^- . It is always well to test the correctness of such simplifying assumptions by subsequent calculation of the quantity neglected. For a more exact treatment it is necessary to estimate values of the ion-activity-coefficients. The ionic strength of the solution, which is the important factor in determining these values, is readily computed from the results of the preliminary calculation. In the following group of problems the exact treatment will not be considered.

Prob. 22. — Concentrations of the Substances Present in the Solution of a Dibasic Acid. — From the ionization-constants given in the table above, calculate by the method just described the molal concentration of each of the substances present in a 0.01 formal solution of tartaric acid at 25°.

Prob. 23. — Determination of the Ionization-Constant for the Second Hydrogen by Reaction-Rate Measurements. — By measuring the conductance of tartaric acid in 0.06–0.01 formal solution, where the ionization of the second hydrogen is negligible, the ionization-constant for the first hydrogen of the acid has been found to be 0.00097 at 25°. The hydrogen-ion concentration in a 0.1 formal solution of sodium hydrogen tartrate, $NaHA$, has been shown by its catalytic effect (in Prob. 16; VI, 6) to be 0.00020

molal. From these data calculate the concentrations (A^-), (HA^-), and (H_2A), and the ionization-constant for the second hydrogen of tartaric acid. (In this case no simplification of the condition-equations is admissible, other than the assumption that the salts $NaHA$ and Na_2A are completely ionized.) Tabulate the molal concentrations of all the substances present in the solution of the sodium hydrogen tartrate.

Determination of the Ionization-Constant for the Second or Third Hydrogen of Acids by Distribution Experiments.

Prob. 24. — A 0.1 volume-formal solution of sodium hydrogen succinate in water is found by experiment to be in equilibrium at 25° with a 0.00187 volume-formal solution of succinic acid in ether. The distribution-ratio of succinic acid between water and ether at 25° is 7.5. *a.* Find the concentration of unionized succinic acid in the aqueous solution of the acid salt. *b.* Calculate the ionization-constant for the second hydrogen. That for the first hydrogen is 6.6×10^{-5} . Neglect the value of (H^+) in the condition-equation. *c.* Show by calculating the value of (H^+) that it was justifiable to neglect it. *Ans. b.* 2.5×10^{-6} .

Prob. 25. — Calculate the ionization-constant at 18° for the third hydrogen of H_3PO_4 (that for the ion HPO_4^{2-}) from the data of Prob. 17 and from the ionization-constants of water and of ammonium hydroxide, which at 18° are 0.58×10^{-14} and 1.7×10^{-5} , respectively.

10. Displacement of One Acid or Base from Its Salt by Another. — One of the most important types of equilibrium in aqueous solution is the partial displacement of one acid or base from its salt by another; for example, that of acetic acid from sodium acetate by formic acid, or that of ammonium hydroxide from ammonium chloride by sodium hydroxide.

Before the mass-action relations involved were fully understood, the extent of the displacement was taken as a measure of the relative *strengths* of different acids or bases; those which are largely displaced from their salts being called weak acids or bases, and those which cause such displacement being called strong acids or bases. It is shown by Probs. 26–29 that the mass-action law and ionic theory give a comparatively simple explanation of this phenomenon in the case of not largely ionized univalent acids or bases; also that the relative strengths of different acids or bases, as shown by their displacements, are deter-

mined by their ionization, weak ones being those which are slightly ionized and strong ones those which are largely ionized.

Displacement of Acids or Bases from their Salts.

Prob. 26. — To a 0.1 formal solution of KNO_2 is added at 25° an equal volume of a 0.1 formal solution of acetic acid. *a.* Calculate the fraction of the potassium nitrite that is converted into potassium acetate. *b.* Calculate the fraction that would be so converted if the acetic acid solution were 1.0 formal (instead of 0.1 formal). *c.* Show by reference to the equilibrium-constant of the ion reaction $\text{NO}_2^- + \text{HC}_2\text{H}_3\text{O}_2 = \text{C}_2\text{H}_3\text{O}_2^- + \text{HNO}_2$ that the correction for ion-activity-coefficients is in this case almost negligible.

Prob. 27. — *a.* For the general case expressed by the equation $\text{B}^+\text{A}^- + \text{HA}' = \text{B}^+\text{A}'^- + \text{HA}$ where the solution is originally c formal in B^+A^- and c' formal in HA' , derive an expression for the fraction x of the salt B^+A^- converted into the salt $\text{B}^+\text{A}'^-$, assuming that the ionization-constants of both acids are so small that the ionization of them in the presence of their salts is negligible. *b.* Derive from this expression the relation between the ionization-constants of the acids and the fractions of the basic constituent that are combined with the two acidic constituents for the case that $c = c'$; and state the principle fully in words.

Prob. 28. — To a liter of 0.1 formal HCl solution is added at 25° a liter of 0.1 formal NH_4OH solution and a liter of 0.1 formal $\text{CH}_3\text{NH}_2\text{OH}$ solution. Calculate the fraction of the acid which combines with each base.

Prob. 29. — A 0.1 formal solution of acetic acid is added to an equal volume of 0.1 formal NaHCO_3 solution at 25° , the carbon dioxide produced being kept above the solution at a pressure of 1 atm. *a.* Calculate the concentrations of the two salts and two acids in the resulting solution, taking 0.0338 as the distribution-constant (*IV*, 28) for CO_2 in water at 25° . *b.* Repeat the calculation for the case where no carbon dioxide is allowed to escape from the solution; and tabulate the two results.

The displacement of acids and bases from their salts can often be determined by measuring the heat effect or the change in volume attending the addition of one acid to the salt of the other acid, or of one base to the salt of the other base. In cases where one of the acids has a color different from that of its salt (as in *Prob. 30*), the displacement can be determined by measuring the attendant color change.

Prob. 30. — Determination of Displacement by Color Measurements. — Violuric acid is a slightly ionized acid whose solution is colorless, while solutions of its salts have a violet color which increases proportionately with the quantity of salt. 25 ccm. of a 0.01 formal solution of violuric acid are placed in each of two tubes of the same diameter; to one tube are added 25 ccm. of a 0.01 formal solution of potassium acetate; and to the other tube is added 0.01 formal KOH solution until on looking down through the tubes the colors are seen to be the same, 13.75 ccm. of the KOH solution being required. *a.* Calculate the fraction of the violuric acid which exists in the first mixture in the form of its salt. *b.* Calculate the ionization-constant of the violuric acid.

An important application of the principles relating to the displacement of acids and bases is that to *buffer solutions*, which are solutions that undergo only a relatively small change in their hydrogen-ion or hydroxide-ion concentrations when there is added to them a moderate proportion of either an acid or base, even one that is largely ionized. These buffer conditions are attained in a mixture of a slightly ionized acid (or base) with its neutral salt (as shown by Prob. 31), and most fully when the two are present in equivalent quantities. They are also attained in a mixture of the salts of a polybasic acid, such as a mixture of NaHCO_3 and Na_2CO_3 , or of NaH_2PO_4 and Na_2HPO_4 .

Prob. 31. — Buffer Solutions. — Assuming the ion-activity-coefficients to be given by Eq. 47 (V, γ), calculate the hydrogen-ion activity and the corresponding pH prevailing in the following mixtures: *a.* a solution 0.1 formal in $\text{HC}_2\text{H}_3\text{O}_2$ and 0.1 formal in $\text{NaC}_2\text{H}_3\text{O}_2$; *b.* one liter of solution *a* into which 0.01 formula-weight of gaseous HCl is introduced; *c.* one liter of solution *a* into which 0.01 formula-weight of solid NaOH is introduced; *d.* a solution 0.0000315 formal in HCl and 0.1 formal in KCl ; *e.* one liter of solution *d* into which 0.01 formula-weight of gaseous HCl is introduced. Tabulate all five results.

The adoption of the pH -scale ($V, 38$) for comparing the hydrogen-ion concentration (or *acidity*) of different solutions has led to a similar scale for comparing the strengths of different slightly ionized acids or bases. Just as the hydrogen-ion-exponent pH of a solution is defined in terms of the hydrogen-ion activity $[\text{H}^+]$ by the equation $pH = -\log [\text{H}^+]$, so the *acid-exponent* pHA of an acid HA , or the *base-exponent* of a base BOH , is defined in terms of its ionization constant K_A ,

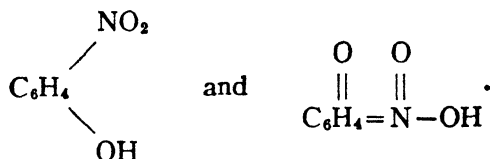
or K_a by the equation $pH = pK_a = -\log K_a$, or $pBOH = pK_b = -\log K_b$. Similarly the symbol pK_w is employed to represent the negative logarithm of the ionization-constant K_w of water.

The use of these conventions is illustrated by the following simple expression for the pH of a buffer solution containing a weak acid HA at concentration c_{HA} formal and its neutral salt BA at concentration c_{BA} formal:

$$pH = pK_a + \log c_{BA}/c_{HA}. \quad (1)$$

It is evident that pH becomes equal to pK_a when c_{BA} is made equal to c_{HA} . Under such conditions the solution has its maximum buffer-action.

11. Neutralization-Indicators. — An acid neutralization-indicator (such as litmus, paranitrophenol, or phenolphthalein) is a mixture of two isomeric acids (HIn' and HIn'') in equilibrium with each other, one of which (HIn'') is present in much smaller proportion, but is so much more ionized than the other (HIn') that when a base BOH is added the salt produced is almost wholly of the form $B^+In'^-$. The substances HIn' and $B^+In'^-$ are different in color from the substances HIn'' and $B^+In''^-$, the color being determined only by the molecular structure of the group In. It follows from these conditions that the indicator acid changes color when converted into its salt. For example, paranitrophenol exists in two isomeric forms to which the following molecular structures are assigned:



The first is the (colorless) form HIn' which is present in predominating proportion in acid solution; the second is the (yellow) form HIn'' , which has a much larger ionization-constant, and hence on the addition of alkali is converted into its (yellow) salt in much larger proportion than the other form.

It can be shown by the mass-action law that the indicator behaves as if it were a single acid HIn whose salt has a different

color from the acid itself; and its behavior can be represented by a single constant K_i called the *indicator-constant*. Namely, by combining the two equilibrium equations (expressed in terms of concentrations):

$$\frac{(\text{HIn}''')}{(\text{HIn}')} = K, \quad \text{and} \quad \frac{(\text{H}^+)(\text{In}''-)}{(\text{HIn}''')} = K'',$$

there results the equation

$$\frac{(\text{H}^+)(\text{In}''-)}{(\text{HIn}')} = KK'' = K_i.$$

Since according to the above statements ($\text{In}'-$) is negligible in comparison with ($\text{In}''-$), and (HIn'') is negligible in comparison with (HIn'), the total indicator acid is substantially equal to (HIn'), and the total indicator salt is substantially equal to ($\text{In}''-$). Hence in the above expression the ratio ($\text{In}''-$)/(HIn') may be replaced by the ratio $x/(1-x)$, where x represents the fraction of the total quantity of the indicator which is in the colored form that exists in alkaline solution. Making this substitution and replacing the hydrogen-ion concentration (H^+) by its activity $[\text{H}^+]$, there results the following fundamental *indicator equation*:

$$[\text{H}^+] \frac{x}{1-x} = K_i. \quad (2)$$

The relations in the case of basic indicators (existing almost wholly in the two differently colored forms $\text{In}'\text{OH}$ and $\text{In}''+\text{A}^-$) are entirely similar to those in the case of acid indicators. Thus, when the equilibrium-constant K_w of water is divided by the ionization-constant K of the reaction $\text{In}'\text{OH} = \text{In}''+ + \text{OH}^-$, there results the following equilibrium equation (expressed in terms of concentrations):

$$\frac{K_w}{K} = K_i = (\text{H}^+) \frac{(\text{In}'\text{OH})}{(\text{In}''+)}.$$

It will be noted that the concentration ratio ($\text{In}'\text{OH}$)/($\text{In}''+$) is equal to $x/1-x$, where as before x represents the fraction of the total quantity of the indicator which is in the colored form that exists in alkaline solution. A basic indicator may therefore be treated as an acid indicator by adopting as the value of its

indicator-constant that calculated by Eq. 2; and it will be so treated in the following considerations.

The color imparted to a solution by the addition of a definite small quantity of indicator is determined by the relative proportions of its acid and alkaline forms, which, in conformity with Eq. 2, are dependent on the hydrogen-ion activity, or pH of the solution. At low values of x , less than about 0.1, the only color discernible is that of the acid form, and the solution is said to react acid to the indicator. Similarly at high values of x , exceeding about 0.9, the color appears to be that of the alkaline form, and the solution reacts alkaline to the indicator. At intervening values of x a mixed or intermediate color is produced, and at $x = 0.5$, pH becomes equal to the indicator-exponent pK_i . Thus, there is for each indicator a characteristic range of pH , largely determined by the indicator-constant and approximately equal to $pK_i \pm 1$, over which the color transition is perceptible to the eye.

TABLE V. INDICATOR-CONSTANTS IN SOLUTIONS OF VARYING IONIC-STRENGTH AT 20°.

Indicator	Color Acid-Alkaline	Range of pH	pK_i at Different Ionic-Strengths			
			0.01	0.05	0.1	0.5
Methyl Orange	Red-Orange Yellow	3.1-4.4	3.46	3.46	3.46	3.46
Bromphenol Blue	Yellow-Purple	3.0-4.6	4.06	4.00	3.85	3.75
Bromcresol Green	Yellow-Blue	3.8-5.4	4.80	4.70	4.66	4.50
Methyl Red	Red-Yellow	4.4-6.2	—	—	5.00	5.00
Chlorphenol Red	Yellow-Red	4.8-6.4	6.15	6.05	6.00	5.9
Bromthymol Blue	Yellow-Blue	6.0-7.6	7.19	7.13	7.10	6.9
Phenol Red	Yellow-Red	6.4-8.2	7.92	7.84	7.81	7.6
Thymol Blue	Yellow-Blue	8.0-9.6	9.01	8.95	8.90	—

From a critical survey by Kolthoff and Rosenblum in *Acid-Base Indicators* (The Macmillan Co., 1937).

In Table V are presented for a series of indicators the colors of the acid and alkaline forms, the pH range for the color transformation, and experimental values of the indicator-exponent in solutions of varying ionic-strength. The apparent variation of pK_i with the ionic-strength is largely due to the fact that in formulating Eq. 2, the effect of ion-attraction on the

activity of the indicator ion (In''^- or In''^+), or on the unionized indicator (HIn' or InOH') was neglected. In precise determinations of pH -values with indicators, failure to take into consideration such variation of the indicator-constant with the concentration and nature of the salts present may lead to serious errors, commonly referred to as *salt-errors*.

One method employed for determining an indicator-constant consists in adding a small but definite quantity of the indicator to a suitable buffer solution of known hydrogen-ion activity (potentiometrically determined) and total salt concentration, and then measuring with the aid of a colorimeter the fraction x of the total indicator in its alkaline form. Conversely, when the indicator-constant is known, color comparisons can be made, as illustrated by Prob. 32, to determine the hydrogen-ion activity, or pH of a solution.

Prob. 32. — Determination of pH by Means of Indicators. —
The following solutions were first prepared:

- (1) 0.100 wf. in $\text{NaC}_2\text{H}_3\text{O}_2$ and 0.065 wf. in HA , a weak acid of unknown ionization-constant K_A .
- (2) 0.08 wf. in NaCl and 0.02 wf. in HCl .
- (3) 0.08 wf. in NaCl and 0.02 wf. in NaOH .

Then nine test tubes of the same diameter were selected for use in making the color comparisons described below. Into one of these tubes was poured a 10 ml. portion of solution (1), into each of four tubes a 10 ml. portion of solution (2), and into each of the remaining tubes a 10 ml. portion of solution (3). Next there was added to each of these solutions a definite number of drops of a dilute standard solution of the sodium salt of bromcresol green. The number of drops added to each solution was as follows:

Drops of Indicator Solution Added.

Solution (1)	10			
Solution (2)	6	5	4	3
Solution (3)	4	5	6	7

The color produced in solution (1) was then compared with that produced by each pair of the other solutions containing a total number of drops of indicator equal to 10 when held one behind the other and viewed against an illuminated white background. (A block of wood drilled with suitable holes was used to exclude light from the sides, and a blank tube containing water was placed behind solution (1).) The color of solution (1) was estimated to fall

between the second and third pairs of the other two solutions shown in the above tabulation. *a.* Find with the aid of Table V the *pH* of solution (1). *b.* From this result and the ionization-constant (1.8×10^{-5}) of acetic acid, calculate a value for the ionization-constant of the acid HA.

12. The Use of Indicators in Acid-Base Titrations. — It is evident from the indicator equation that in the titration of an acid with a base an end-point will be reached when the hydrogen-ion concentration (H^+) becomes so reduced that a considerable fraction x of the indicator is transformed into its salt; also that the observed end-point will be correctly located only if this transformation occurs when equivalent quantities of acid and base are present, and that the sharpness of the end-point will depend on how fast the hydrogen-ion concentration changes in this region with the quantity of base added. Hence, in order to determine how an acid of any known ionization-constant will behave on titration and in order to select the most suitable indicator, it is necessary to know how the hydrogen-ion concentration varies when a largely ionized base is progressively added.

Table VI contains values of *pH* prevailing at 25° in solutions of acids of ionization-constants 10^{-3} , 10^{-5} , 10^{-7} , and 10^{-9} when the ratio B/A of the quantity of strong base added to the quantity of the acid present has the values given in the first column (the original concentration of the acid and that of the standard base being 0.2 normal).

TABLE VI. CHANGE OF pH ON NEUTRALIZATION OF DIFFERENT ACIDS.

Ratio B/A	Values of <i>pH</i> Near the Theoretical End-Point			
	$K_A = 10^{-3}$	$K_A = 10^{-5}$	$K_A = 10^{-7}$	$K_A = 10^{-9}$
0.980	4.70	6.70	8.70	10.62
0.990	5.00	7.00	9.00	10.80
0.995	5.30	7.30	9.30	10.92
0.998	5.70	7.70	9.62	10.96
1.000	8.00	9.00	10.00	11.00
1.002	10.30	10.30	10.40	11.05
1.005	10.70	10.70	10.70	11.10
1.010	11.00	11.00	11.00	11.22
1.020	11.30	11.30	11.30	11.40

These numbers are also the values of the hydroxide-ion-exponent pOH for the case that a 0.2 normal solution of a base having an ionization-constant equal to 10^{-3} , 10^{-5} , 10^{-7} , or 10^{-9} is titrated with a 0.2 normal solution of a strong acid (like HCl), provided the numbers in the first column denote the ratio (A/B) of the quantity of acid to the quantity of base. Thus, when the ratio A/B is 0.98, the value of pOH is 4.70 for a base for which $K = 10^{-3}$.

The method of calculating such hydrogen-ion concentrations in the neighborhood of the theoretical end-point is shown in Prob. 33.

Prob. 33. — Titration of a Weak Acid with a Strong Base. —

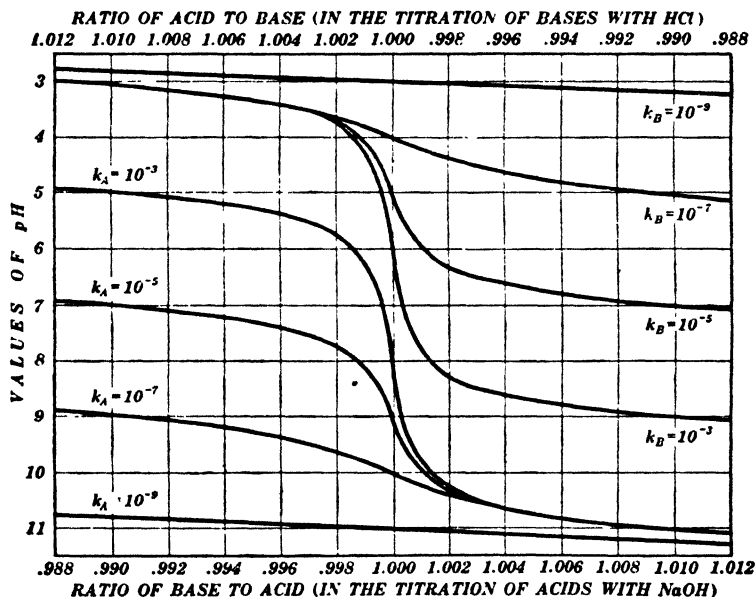
a. A 100 ml. portion of a 0.2 normal solution of an acid whose ionization-constant is 10^{-7} is titrated at 25° with 0.2 normal KOH solution. Assuming the ions to behave as perfect solutes, calculate the H^{+} concentration and the corresponding pH in the mixture at the start, and also when 10.0, 50.0, 90.0, 99.0, 99.5, 99.8, and 100.0 ccm. of the KOH solution have been added. Regard at first each mixture as one of the salt $K^{+}A^{-}$ and the acid HA such as would result if the added base were completely neutralized, and then calculate the hydrolysis of the salt in such a mixture. Take this hydrolysis into account where necessary in calculating the H^{+} concentration. Assume the volume of the mixture to be always 200 ccm. when within one percent of the end-point. *b.* Calculate the H^{+} concentration and pH values when 100.2, 100.5, 101.0, and 110.0 ccm. of the KOH solution have been added. In this case regard at first each mixture as one of the salt $K^{+}A^{-}$ in presence of a slight excess of the base $K^{+}OH^{-}$. *c.* Plot the pH values thus computed as ordinates against the corresponding ratios of base to acid as abscissas.

In Figure 1, as in the diagram of Prob. 33, the pH values given in Table VI are plotted as ordinates against the ratio of base to acid as abscissas for each of the four acids, and for four bases with the same ionization constants. At the top of the figure is a scale of the corresponding ratios of acid to base.

Prob. 34. — Titration of Acids and Bases. — a. From a study of Figure 1 tabulate the values between which the indicator exponent pK_i must lie in order that the titration of each of the four acids and four bases may be correct within 0.2%, assuming that the indicator is 9% transformed. *b.* Show from the plot what percentage error would be made in using phenolphthalein

($K_I = 10^{-10}$) in titrating an acid for which $K_A = 10^{-6}$ when the fraction of the indicator transformed is 1%, 9%, and 50%; also in titrating an acid for which $K_A = 10^{-7}$ when the fraction of the indicator transformed is 9% and 50%. *c.* If the acid for which $K_A = 10^{-9}$ were titrated with the aid of an indicator for which $K_I = 10^{-12}$ (which is not far from the value for trinitrobenzene), what error would be made when the fraction of the indicator transformed is 5%, 9%, and 15%? (Note that in a titration carried out in the usual way the fraction transformed is not determined more closely than this. Note also that an error in the

FIGURE 1. CHANGE OF pH IN THE TITRATION OF ACIDS AND BASES.



assumed value of the indicator-constant would affect the results in the same way as a variation in the fraction transformed.)

Prob. 35. — a. Calculate the value of pH at the end-point in titrating with phenolphthalein ($K_I = 10^{-10}$) when the fraction x of it transformed is 5% and 20%; with rosolic acid ($K_I = 10^{-8}$) when x is 5% and 20%; with paranitrophenol ($K_I = 10^{-7}$) when x is 1% and 20%; and with methyl orange ($K_I = 5 \times 10^{-4}$) when x is 80% and 95% (these being about the ranges practicable in a titration). *b.* Draw in pencil on the figure in the book horizontal lines representing the two limiting values of pH for each of the four indicators. Letter and shade lightly the four zones on the

figure so as to show for each indicator the limiting values of pH between which the end-point is commonly chosen.

Prob. 36. — With the aid of the figure show which of these indicators would give a result accurate within 0.2–0.3% in titrating *a.* NH_4OH with HCl ; *b.* HNO_2 with KOH ; and *c.* aniline ($C_6H_5NH_2$) with HCl .

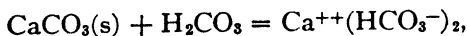
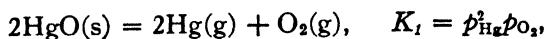
Prob. 37. — *Titration of the Successive Hydrogens of Polybasic Acids.* — A solution 0.2 formal in H_3PO_4 is titrated with 0.2 formal $NaOH$ solution. With the aid of the ionization-constants, calculate the H^+ ion concentration after the addition of enough base to be equivalent, *a.* to 99% of the first hydrogen of the acid; *b.* to 1% of the second hydrogen; *c.* to 99% of the second hydrogen; *d.* to 1% of the third hydrogen. *e.* By reference to the diagram determine what indicators could be used for titrating the first hydrogen and the second hydrogen of the acid.

IV. THE MASS-ACTION LAW FOR REACTIONS INVOLVING SOLID PHASES.

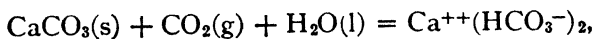
13. Form of the Mass-Action Expression. — When a substance present as a solid phase is involved in a reaction with gaseous substances, that substance has in the gaseous phase of all equilibrium mixtures at any definite temperature the same pressure (or more exactly stated, the same fugacity), namely, one equal to the vapor-pressure (or fugacity) of the solid substance. Similarly, when a substance present as a solid phase is involved in a reaction with dissolved substances, it has in the liquid phase of all equilibrium mixtures at any definite temperature the same concentration (or more exactly stated, the same activity), namely, one equal to its concentration (or activity) in a solution saturated with the solid substance and containing no other solutes. Hence the fugacity in the gaseous phase or the activity in the liquid phase of any substances which are also present as solid phases may be left out in formulating the mass-action expression; their constant fugacities or activities being understood to be included in the equilibrium-constant.

In these statements is concealed the slightly inexact assumption that the molar free energy of the solid substance, and hence also its activity (as defined in IV, 43), is independent of the pressure to which it is subjected. The consequent error is readily shown, however, to be negligible when the applied pressure does not differ greatly from 1 atm., which is the pressure at which the solid substance is usually considered to be in its standard state of unit-activity. In mass-action formulation it is convenient to refer the activity of any solid substance to this standard state, thereby making it equal to unity, regardless of whether the other substances involved in the reaction are in a gaseous or a liquid phase. It should be noted, however, that when such a substance is present in solid solution, its activity may be considerably less than unity, just as is the activity of water, or other solvent, in a concentrated liquid solution.

The following examples are presented to illustrate the form of the equilibrium-constant for several types of reaction in which a solid substance is involved. For simplifying the formulation, the laws of perfect gases and solutions are assumed.



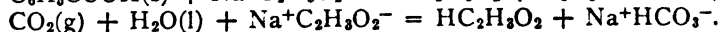
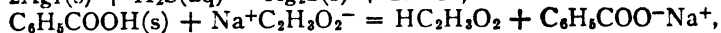
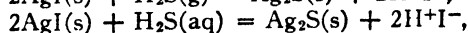
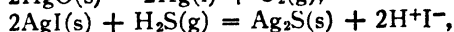
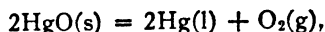
$$K_2 = (\text{Ca}^{++})(\text{HCO}_3^-)^2/[\text{H}_2\text{CO}_3],$$



$$K_3 = (\text{Ca}^{++})(\text{HCO}_3^-)^2/p_{\text{CO}_2}.$$

As here illustrated, solid, liquid, and gaseous substances occurring in chemical equations are indicated by attaching to their formulas (s), (l), and (g), respectively, when it is important to show the state of aggregation. Substances in solution are written either without any such addition to their formulas or with the addition of a parenthesis to indicate the dissolved state; for example, $\text{CO}_2(\text{aq})$ to indicate CO_2 in aqueous solution. As previously explained (VII, 8), the standard reference states of unit-activity of dissolved CO_2 and H_2CO_3 are so defined that in any moderately dilute solution of carbonic acid, $[\text{CO}_2] = [\text{H}_2\text{CO}_3] = (\text{CO}_2) + (\text{H}_2\text{CO}_3)$. In consequence the equilibrium-constant of the reaction, $\text{CaCO}_3(s) + \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(l) = \text{Ca}^{++} + 2\text{HCO}_3^-$, is identical in value with K_2 above, and the ratio K_3/K_2 is equal to the constant of Henry's law of distribution of carbon dioxide between water and a gas phase.

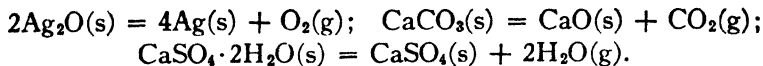
Prob. 38. — Formulation of Equilibrium-Constants of Heterogeneous Chemical Reactions. — a. Formulate the mass-action expression for each of the following reactions:



b. State the significance of the ratio of K_1 in the above text to the equilibrium-constant of the first reaction. *c.* Show a relation between the equilibrium-constants of the second and third reactions and the distribution-constant of H_2S between water and a gas phase. *d.* Evaluate the equilibrium-constant at 25° of the fourth reaction from the solubility of benzoic acid in pure water which is 0.0276 volume-formal, and other related constants, whose values have been previously given. (Note that the ionization of benzoic acid in its saturated solution in pure water is not negligible.) *e.* Evaluate the equilibrium-constant at 25° of the fifth reaction from equilibrium data previously given.

14. Reactions Involving Solid and Gaseous Substances.

— The simplest type of the reactions involving solid and gaseous substances is that in which only one substance is present in appreciable quantity in the gaseous phase. Examples of this type are:



The mass-action expression for this case is simply $p = K$, which signifies that at any definite temperature there is only one pressure of the gas at which there can be equilibrium. This pressure is called the *dissociation-pressure* of the substance undergoing decomposition (thus of the silver oxide, the calcium carbonate, or the gypsum). If the pressure of the gas is kept larger than this pressure, the reaction takes place completely in one direction, with the result that the gas is entirely absorbed; and if the pressure is kept smaller, the reaction takes place completely in the other direction, with the result that the dissociating substance completely decomposes. This important characteristic of reactions of this type will be fully considered in the next chapter.

Other types of reactions, involving equilibrium between solid substances and two or more gaseous substances, are illustrated by the following problems.

Dissociation of Solid Substances Producing Two Gaseous Substances.

Prob. 39. — When solid NH_4SH is placed in a vacuous space at 25° a pressure of 500 mm. is developed, owing to the dissociation of the salt, which is itself not appreciably volatile, into NH_3 and H_2S . If solid NH_4SH were introduced into a space which already contained H_2S at a pressure of 300 mm., what increase of pressure would result?

Prob. 40. — The equilibrium-constant (expressed in atmospheres) of the reaction $2\text{NaHCO}_3(\text{s}) = \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ at 100° is 0.23. A current of moist carbon dioxide is passed at 1 atm. over solid sodium hydrogen carbonate (in order to free it from adhering water). How great must the mol-fraction of the water in the gas be to prevent decomposition of the salt?

Prob. 41. — When solid mercuric oxide is heated in an evacuated tube to 357° in the vapor of mercury boiling at 1 atm., a pressure of 86 mm. is produced in the tube owing to dissociation of

the oxide into mercury vapor and oxygen. Assuming that a mixture of solid mercuric oxide and liquid mercury is heated in the same way, calculate the partial pressure of the oxygen in the tube. *Ans.* 0.163 mm.

Prob. 42. — Equilibrium of the Producer Gas Reaction. — In one stage of the manufacture of producer gas a current of air at 1 atm. is passed through coke at a high temperature. Calculate the mol-fractions of CO_2 and CO in the gas issuing at 1000° , assuming equilibrium to be reached. The equilibrium-constant for the reaction $\text{C(s)} + \text{CO}_2\text{(g)} = 2\text{CO(g)}$ at 1000° is 140.

*Dissociation-Pressure in Relation to
Equilibrium-Constants.*

Prob. 43. — At 1120° the gaseous mixture in equilibrium with iron and ferrous oxide consists of 54 mol-percent of H_2 and 46 mol-percent of H_2O . Calculate the dissociation-pressure of ferrous oxide, referring to Prob. 7 (VII, 2) for the additional data needed. *Ans.* 2.54×10^{-13} atm.

Prob. 44. — In the blast-furnace process iron is reduced by the reaction $\text{FeO(s)} + \text{CO(g)} = \text{Fe(s)} + \text{CO}_2\text{(g)}$. Calculate the least quantity of carbon monoxide that could reduce one formula-weight of FeO at 1120° using the dissociation-pressure of ferrous oxide found in Prob. 43 in conjunction with the data of Prob. 7.

15. Reactions Involving Solid and Dissolved Substances.

Solubility Effects. — Calculation of the effect of an added solute on the solubility of any definite substance is conveniently made by the following general procedure. Compute first the solubility assuming the laws of perfect solutions, and then, if it is judged necessary, repeat the calculation applying corrections for deviations from these laws through the use of activity-coefficients. The preliminary calculation involves consideration of the chemical nature of the effect, whereas the final calculation necessitates in addition a consideration of the effect of ion-attraction or other physical effect on the activity of the dissolved substances taking part in the reactions of solution.

Under the assumption of the laws of perfect solutions, the fundamental principle determining the solubility of an unionized or slightly ionized substance in the presence of other solutes is that the concentration of this substance, or of its unionized part if its ionization is not negligible, has the same value at any definite temperature in any solution saturated with respect to

that substance, whatever other solutes may be present. In general, the effect of ion-attraction on this, or any other electrically neutral species, is to increase its activity at a definite concentration. Consequently addition of electrolyte produces, in the absence of any chemical action, a decrease in the solubility of a substance of this type. The magnitude of this salting-out effect, already referred to under gas solubility (IV, 28), varies greatly with the nature of the added electrolyte. As a rule it may be considered to be negligible at ionic strengths less than 0.1 molal, but in concentrated salt solutions, may become very large. In the following problems the salting-out effect should be neglected.

Solubility-Increase Due to Complex-Formation.

Prob. 45. — At 25° the solubility of iodine (I_2) in water is 0.0013 volume-formal, and its solubility in 0.1 vf. KI solution is 0.0517 volume-formal, the increase being due to the reaction $I_2(s) + I^- = I_3^-$. *a.* Calculate the solubility of iodine in 0.01 vf. KI solution assuming the laws of perfect solutions. *b.* Show how the result would be changed by taking the effect of ion-attraction into consideration. *c.* Formulate a general relation between the solubility s of I_2 and the concentration c of KI at 25°.

Prob. 46. — Calculate the solubility of $HgCl_2$ in 0.1 vf. NaCl solution at 25° from the results of the distribution experiments of Prob. 46 (I', 31), and from the fact that its solubility in water at 25° is 0.263 volume-formal.

Prob. 47. — *Solubility-Increase Due to Metathesis.* — *a.* Calculate the solubility of benzoic acid C_6H_5COOH in 0.1 vf. $NaC_2H_3O_2$ solution at 25° from its solubility in water (0.0276 vf.) and other equilibrium data previously given.

The mass-action law applied to perfect solutes evidently requires, in all solutions saturated with the same solid substance, that not only the concentration of the unionized substance have the same value, but also that the product of the ion-concentrations raised to the appropriate power have the same value, whatever other substances may be present. Thus at any definite temperature in any aqueous solution saturated with silver sulfate, whether it is present alone or with another solute, such as silver nitrate or ammonia, the first of these principles requires that (Ag_2SO_4) have a definite value; and the second principle requires that the product $(Ag^+)^2(SO_4^{--})$ also have a definite value.

The saturation value of the ion-concentration product is commonly called the *solubility-product*; and the principle expressing its constancy is called the *solubility-product* principle.

The treatment of solubility effects in the case of a slightly soluble salt, strong acid, or strong base is much simplified by the fact that the concentration of its unionized part (for example (Ag_2SO_4) in the case just cited) is considered to be zero. Hence for such substances the solubility-product principle is employed for the preliminary approximate calculation.

The effect of ion-attraction on the solubility of strong electrolytes is appreciable even at small ionic-strengths. In contrast to the solubility-decrease observed with non-electrolytes, the solubility of a strong electrolyte is increased by the addition of moderate quantities of a second electrolyte which neither reacts chemically with the dissolved substance nor has an ion in common with it. Thus, as illustrated by the data of Prob. 48, thallous chloride is more soluble in dilute solutions of potassium nitrate than it is in pure water. The problem also illustrates a method for determining the mean activity-coefficient of the ions of a slightly soluble salt.

Prob. 48. — Evaluation of Ratios of Activity-Coefficients from Solubility Effects. — a. Calculate the ratio of the mean activity-coefficients of the ions of thallous chloride at 25° in the following solutions: Its saturated solution in water which is 0.01612 volume-formal in TlCl ; and its saturated solution in 0.1 vf. KNO_3 which is 0.01961 volume-formal in TlCl . *b.* Calculate by the theoretical dilute solution ion-attraction equation the absolute value of the activity-coefficients of the ions of TlCl in its saturated solution in pure water. *c.* By combining this value with the ratio found in *a*, calculate the mean ion-activity-coefficient of TlCl in the potassium nitrate solution, and compare it with that calculated by theory.

Prob. 49. — Solubility-Increase by Ion-Attraction Effect. — Calculate the solubility of AgBrO_3 at 25° in 0.0125 vf. $\text{Ba}(\text{NO}_3)_2$ from its solubility in pure water which is 0.00806 volume-formal. The solubility determined by experiment is 0.00909 vf.

The following problems illustrate the commonly occurring changes in the solubility of salts, strong bases, and strong acids caused by various kinds of chemical effects. In solving these problems, calculate the ion-activity-coefficients needed for

the exact treatment by the theoretical dilute solution ion-attraction equation.

Solubility-Decrease by Substances with a Common Ion.

Prob. 50. — Calculate the solubility of AgBrO_3 in 0.0346 vf. AgNO_3 solution from its solubility in water, which is 0.00806 volume-formal. For evaluating the ionic strength, use the solubility value calculated under the assumption that the ions behave as perfect solutes. The experimentally determined solubility is 0.00216 vf.

Prob. 51. — The solubility of KClO_4 in water at 25° is 0.148 volume-formal. Calculate its solubility in 0.100 vf. KCl solution. Assume the mean ion-activity-coefficients of KClO_4 to be the same in the two saturated solutions. Compare the result with the value 0.112 volume-formal experimentally determined.

Prob. 52. — *a.* Derive an expression for the solubility s of AgCl in a dilute NaCl solution of concentration c in terms of its solubility s_0 in water, assuming the ions to behave as perfect solutes. *b.* Calculate the ratio s/s_0 for $c = s_0$; for $c = 2s_0$; and for $c = 10s_0$.

Prob. 53. — The solubility of Ag_2SO_4 in water at 25° is 0.0268 volume-formal. *a.* Calculate its solubility in 0.05 vf. AgNO_3 , and *b.* in 0.025 vf. K_2SO_4 , solving in each case the cubic equation by trial. For evaluating the ionic strength, use the solubility calculated under the assumption that the ions behave as perfect solutes. *c.* Record these four calculated solubilities with the two values experimentally determined, which are 0.0142 vf. and 0.0247 vf. respectively.

Prob. 54. — The solubility of $\text{Mg}(\text{OH})_2$ in water at 18° is 1.4×10^{-4} volume-formal. *a.* Calculate its solubility in 0.002 vf. NaOH solution. *b.* Calculate its solubility in 0.001 vf. MgCl_2 solution. In both cases assume the laws of perfect solutions.

Prob. 55. — *Solubility-Increase through Metathesis.* — The solubility of $\text{Mg}(\text{OH})_2$ in water at 18° is 1.4×10^{-4} volume-formal. *a.* Calculate its solubility in 0.002 vf. NH_4Cl solution. Neglect the concentration of OH^- in comparison with the sum of the concentrations of NH_4OH and NH_3 and assume the laws of perfect solutions. *b.* Calculate the ratio of (OH^-) to $(\text{NH}_4\text{OH}) + (\text{NH}_3)$ in the saturated solution in order to test the simplifying assumption above made. *Ans. a.* 8.6×10^{-4} .

Prob. 56. — *Solubility-Increase through Complex-Formation.* — The solubility of AgCl in water at 25° is 1.30×10^{-5} volume-formal. Calculate an approximate value for its solubility in 0.1 volume-formal NH_3 solution. There is formed a complex ion by the reaction $\text{Ag}^+ + 2\text{NH}_3 = \text{Ag}(\text{NH}_3)_2^+$, its equilibrium-

constant (commonly called the complex-constant) having the value 1.4×10^7 . *Ans.* 0.0044.

Conversion of One Solid Substance into Another.

Prob. 57. — The solubility of silver thiocyanate is 1.2×10^{-6} volume-formal and that of silver bromide is 0.7×10^{-6} volume-formal at 25° . *a.* Calculate the equilibrium-constant of the reaction $\text{AgSCN(s)} + \text{K}^+\text{Br}^- = \text{AgBr(s)} + \text{K}^+\text{SCN}^-$. *b.* If 8.3 g. of solid AgSCN are treated with 200 ccm. of 0.1 formal KBr solution, what proportion of the silver salt is converted into bromide? *c.* What volume of the 0.1 formal KBr solution would convert the solid AgSCN completely into AgBr? *d.* With what mixtures of potassium thiocyanate and potassium bromide could the silver thiocyanate be treated without any change taking place?

Prob. 58. — Determine the ratio of carbonate to hydroxide in the solution obtained by digesting at 25° a 0.1 formal Na_2CO_3 solution with excess of solid Ca(OH)_2 (as in the technical process of causticizing soda). The solubility of calcium hydroxide in water is 0.020 formal, and the product $(\text{Ca}^{++}) \times (\text{CO}_3^{--})$ has the value 3×10^{-9} in water saturated with calcium carbonate. The calcium dissolved in the mixture is small in comparison with the sodium.

V. THE EFFECT OF TEMPERATURE ON THE
EQUILIBRIUM OF CHEMICAL
REACTIONS.

16. Effect of Temperature on the Equilibrium-Constant of a Reaction Involving Gases. — The standard free energy ΔF° of any chemical reaction at any definite temperature T may be calculated, as previously shown (IV, 46), from its equilibrium-constant K by the simple equation, $-\Delta F^\circ = R T \ln K$. It may be recalled that the standard free energy of a reaction is defined as the increase in free energy attending the chemical change when initially, each of the reactants, and finally, each of the reaction-products is in some arbitrarily chosen standard state to which its activity is referred in evaluating the equilibrium-constant. The corresponding heat-content increase, designated by the symbol ΔH° , is commonly called the heat of the reaction.

In the case of any reaction between gases in a homogeneous system, or between solids and gases in a heterogeneous system, these standard states, as defined in IV, 44, correspond to a pressure of one atmosphere at each temperature; and hence, in calculating the standard free energy of the reaction by the above equation, the equilibrium-constant is expressed in terms of the pressures in atmospheres, or more exactly stated, the fugacities of the gaseous substances. By substituting this value of ΔF° , and the corresponding value of ΔH° , in the second-law free energy equation (Eq. 65; II, 32), there is obtained the following relation, commonly called the *van't Hoff equation* (1884) expressing the effect of temperature on the equilibrium-constant K of any reaction involving gases.

$$d \ln K = \frac{\Delta H^\circ}{R T^2} dT. \quad (3)$$

Prob. 59. — Qualitative Principle Expressing the Effect of Temperature on Chemical Equilibrium. — Derive from the van't Hoff equation a principle showing how the direction in which an equilibrium is displaced by increase in temperature is related to the sign of the heat-effect attending the reaction.

Applications of the Qualitative Principle.

Prob. 60. — Show how the equilibrium in a gaseous mixture of Cl_2 , HCl , O_2 , and H_2O at 18° would be displaced by increasing

the temperature. The heat of formation at 18° of 1HCl(g) is $-22,060$ cal. and that of $1\text{H}_2\text{O(g)}$ is $-57,800$ cal.

Prob. 61. — The dissociation-pressure of solid CaCO_3 (and of all other solid substances which dissociate into one or more gaseous products) increases with rising temperature. State whether heat is absorbed or evolved when the dissociation takes place at constant temperature.

In order to integrate the van't Hoff equation, the heat-content increase ΔH° must be expressed as a function of the temperature.

This temperature function is usually derived, in the way previously shown (*II, 14*), from a knowledge of the heat of the reaction at some one temperature, and of the heat-capacities at constant pressure of the reactants ($A, B, \dots$) and of the reaction-products ($E, F, \dots$). Thus the function may always be obtained by integrating the following differential equation, in which ΔC represents the difference between the heat-capacity (equal to $C_E + C_F, \dots$) of the system in its final state and its heat-capacity (equal to $C_A + C_B, \dots$) in its initial state:

$$d(\Delta H^\circ) = \Delta C \cdot dT.$$

The integration can evidently be carried out when ΔC is known to be constant or when it can be expressed as a function of the temperature of the form $\Delta C = \Delta C_0 + \alpha T + \beta T^2$, where ΔC_0 , α , and β are constants which are based on experimental determinations at a series of temperatures of the heat-capacities of the substances involved in the reaction. The corresponding integrated form of the equation (*Prob. 37; II, 14*) may be written as follows:

$$\Delta H^\circ = \Delta H_0 + \Delta C_0 T + \frac{1}{2} \alpha T^2 + \frac{1}{3} \beta T^3. \quad (4)$$

The constant of integration ΔH_0 can evidently be calculated from the heat of the reaction ΔH° at some definite temperature T , and the other empirical constants in the equation. The equation is limited to the range of temperature for which the heat-capacity function is valid.

Prob. 62. — *Integration of the van't Hoff Equation.* — Integrate the van't Hoff equation between the limits T_1 and T_2 , K_1 and K_2 for the following cases: *a.* When ΔC is zero and therefore

ΔH° does not vary with temperature; *b.* When ΔC has a finite value which does not vary with temperature; *c.* When ΔC varies with temperature, and hence also ΔH° as shown by Eq. 4.

In numerical applications of the van't Hoff equation, in order to guard against errors in the sign of the heat-content increase and in its value with respect to the multiple chosen, the reaction under consideration should first be formulated in a definite chemical equation and then values of K , ΔH° and ΔC should be adopted in conformity with it. For the heat-capacities of some important gaseous substances see Table II (II, 14).

Applications of the van't Hoff Equation to the Equilibrium of Gas Reactions.

Prob. 63. — It has been found that when dry air (containing 21.0 mol-percent of oxygen and 78.0 mol-percent of nitrogen) is kept at 1957°C till equilibrium is reached, 4.3% of the oxygen present is converted into nitric oxide. Calculate the percentage that would be so converted at 3000°C. The formation of 1NO(g) from nitrogen and oxygen at 18°C is attended by a heat-absorption of 21,600 cal.

Prob. 64. — When a mixture of 0.49 mol of O₂ and 1.00 mol of HCl is kept at 386°C and 1 atm. in contact with solid cuprous chloride (which acts as catalyst) till equilibrium is reached, 80% of the HCl is converted to Cl₂ and H₂O. *a.* Calculate ΔF° , the standard free energy of the reaction $4\text{HCl(g)} + \text{O}_2\text{(g)} = 2\text{H}_2\text{O(g)} + 2\text{Cl}_2\text{(g)}$ at 386°C. *b.* Formulate as a function of the absolute temperature the heat of this reaction ΔH° , using the heat-content data of Prob. 60, and the heat-capacity data of Table II (II, 14). *c.* Substitute this result in the second-law free energy equation, and by integration (see Eq. 66; II, 32) derive a general equation expressing the standard free energy of the reaction ΔF° as a function of the absolute temperature. *d.* Calculate by means of this equation the standard free energy of the reaction at 25°, and the corresponding value of the equilibrium-constant.

Prob. 65. — Calculate from the heat data given below and the values of the heat-capacities of gaseous substances previously given: *a.* the heat of dissociation of 1HgO(s) into mercury vapor and oxygen at 357°C; *b.* a temperature-function expressing the heat-content increase attending this dissociation above 357°C; *c.* the dissociation-pressure of solid mercuric oxide at 390°C. The heat of formation of 1HgO(s) at 18°C is - 21,600 cal. The vaporization of 1Hg(l) at its boiling-point (357°C) absorbs 14,160 cal. The mean value of the atomic heat-capacity of liquid mercury between 18° and 357°C is 6.6 cal. per degree; and the heat-

capacity of 1HgO(s) may be taken as $9.0 + 0.006 T$ above 18°C . The dissociation-pressure of mercuric oxide at 357°C is 86 mm.

17. Effect of Temperature on the Equilibrium-Constant of a Reaction Involving Solutes. — In the case of a reaction taking place in aqueous solution, the standard state (*IV*, 44) to which the activity of each solute is usually referred in evaluating the equilibrium-constant corresponds to a concentration 1 weight-molal. Now, since the weight-molality of a substance does not vary with the temperature when the solution is heated at constant pressure, the expression, $\Delta F^\circ = R T \ln K$, for the free energy of the reaction may, as in the case of a reaction involving gases, be substituted in the second-law free energy equation, and there again results the van't Hoff equation. This equation is also applicable to chemical changes between solids and solutes, since by definition the standard state of unit-activity of a solid at any definite temperature is 1 atm. For similar reasons, it applies also to changes in which the solvent (thus the water in aqueous solutions) enters into reaction with solutes.

The integration of the equation evidently involves the expression of the heat of the reaction (at infinite dilution) as a function of the temperature. Since in the case of solutions the temperature interval often is not large, the increase in heat-content can frequently be regarded as constant; and it is to be so regarded in the following problems unless otherwise stated. When this is not admissible, its variation with the temperature must be known. This is usually derived from direct determinations of the heat-effects attending the reaction at two or more different temperatures; for there is likely to be a large error involved in calculating it from the partial molar heat-capacities of the solutes, since they form only a small part of the total heat-capacity of the solution.

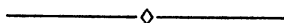
Prob. 66. — Application of the Qualitative Principle. — State the conclusions in regard to the heat of solution that can be drawn from the facts that as a rule the solubility in water of gaseous substances is decreased, and the solubility of solid substances is increased, by an increase of temperature.

Prob. 67. — Effect of Temperature on the Ionization of Water. — The neutralization of largely ionized univalent acids and bases in fairly dilute solution has been found by direct

measurements at 2° , 10° , 18° , 26° , and 34° to evolve $14,750 - 52 t$ cal. at the centigrade temperature t . The value of the ionization-constant of water at 25° is 1.00×10^{-14} . Calculate its value at 0° .
Ans. 0.1×10^{-14} .

Prob. 68. — Effect of Temperature on the Hydrolysis of Salts. — Calculate the hydrolysis of 0.1 wf. NH_4CN at 0° from its hydrolysis (42%) at 25° and from the fact that on mixing at 25° a solution containing 0.2 NH_3 and 1000 g. of water with one containing 0.2 HCN and 1000 g. of water and bringing the mixture back to 25° there is a heat evolution of 152 cal.

Prob. 69. — Effect of Temperature on Solubility. — The solubility of silver chloride in water is 1.10×10^{-5} formal at 20° and 15.2×10^{-5} formal at 100° . *a.* State just what heat-quantity can be computed from these data, and calculate its value. *b.* State by what thermochemical measurement it could be determined experimentally.



CHAPTER VIII

EQUILIBRIUM OF CHEMICAL SYSTEMS IN RELATION TO THE PHASES PRESENT

I. THE PHASE RULE.

1. The Phase Rule and Its Inductive Derivation. — In this chapter will be considered various types of diagrams which show how at equilibrium the nature, the quantity, and the composition of the phases of a series of systems of the same qualitative composition vary when the composition of the system as a whole and the pressure and temperature are varied. There will first be presented a general principle called the *phase rule* (*Gibbs, 1875*) which furnishes a basis for the classification of the various types of equilibrium.*

The phase rule states that in any system the sum of the number of phases (P) and of the variance (V) is greater by two than the number of components (C); that is,

$$P + V = C + 2. \quad (1)$$

This principle is applicable to systems consisting of any number of components. Its limitations will be made clear by the following statements and by its derivation in Prob. 1, or in *VIII, 3*.

In order that the intensive properties (*I, 10*) of any one phase of a system, such as its density, specific conductance, index of refraction, etc., may be fully determined, it is necessary to specify, in addition to the proportions of its components, any external factors which may effect these properties. The only external factors which commonly have an appreciable influence are pressure and temperature. In the derivation of the phase rule, these factors are alone taken into account, and their values are assumed to be uniform throughout all phases of the system. Furthermore, it is assumed that none of the phases are in the dispersed (or colloid) state of aggregation (*I, 12*).

* It is desirable to review here the definition of the components and phases of systems (*I, 16*), the concept of equilibrium in general (*I, 17*), and that of the variance of a system (*I, 18*).

Now it has already been shown (*I, 18*) that any one-component system which exists as a single phase is bivariant; one which exists in two phases is univariant; and one which exists in three phases is nonvariant. In other words, for one-component systems the sum of the phases and the variance is always three as required by the phase rule. The extension of this rule to include systems of more than one component is justified by the considerations of the following problem.

Prob. 1. — Inductive Derivation of the Phase Rule. — Consider the following systems existing in the phases indicated.

- (1) Solution of C_2H_5OH and H_2O .
- (2) Two solutions, $CHCl_3$ in H_2O , and H_2O in $CHCl_3$.
- (3) Two solutions, $CHCl_3$ in H_2O , and H_2O in $CHCl_3$; and their vapors.
- (4) Two solutions, $CHCl_3$ in H_2O , and H_2O in $CHCl_3$; their vapors; and ice.
- (5) Solution of C_2H_5OH , H_2O , and $HC_2H_3O_2$.
- (6) Solution of C_2H_5OH , H_2O , and $HC_2H_3O_2$, and their vapors.
- (7) Two solutions formed by dissolving NH_3 in a heterogeneous mixture of solvents, H_2O and $CHCl_3$.
- (8) Two solutions, described in (7); and their vapors.

a. Upon the basis of the principles already considered relating to solubility, vapor-pressure, and freezing-point, name definitely certain factors the specification of whose values will fully determine all the intensive properties of each phase of these systems.
b. Make a table showing the number of components, the number of phases, the variance, and the sum of the number of phases and the variance, for each of these systems. c. Formulate a generalized statement of the results.

The phase rule enables the number of phases that can exist under specified conditions to be predicted. The usefulness of the rule itself is, however, often exaggerated. Of primary importance in the treatment of the equilibrium conditions of systems in relation to the phases present are the methods of representing those conditions by diagrams, as described in later articles of this chapter.

Prob. 2. — Number of Phases Permitted by the Phase Rule. — Sodium carbonate and water form solid phases of the composition $Na_2CO_3 \cdot H_2O$, $Na_2CO_3 \cdot 7H_2O$, and $Na_2CO_3 \cdot 10H_2O$. a. State how many of these hydrates could exist in equilibrium with the solution and ice under a pressure of 1 atm. b. State how many

of these hydrates could exist in equilibrium with water-vapor at 30°.

2. Discussion of the Concept of Components. — The substances to be regarded as the components, and correspondingly the number of components, are obvious in cases, like those already considered, in which there is no transformation of the components into other chemical substances. In cases where a chemical action occurs, the term component requires to be more specifically defined, which may be done as follows. It is evident from the preceding derivation of the phase rule (and from that in VIII, 3) that in general any substances may be selected as the *components*, the specification of the relative quantities of which in any phase suffices to determine fully the composition of that phase; the components, moreover, being such that this is true whatever phase of the system is considered. This definition is illustrated by the following examples.

The composition of a gaseous phase containing hydrogen, oxygen, and water-vapor in equilibrium with one another at any definite temperature and pressure is fully determined by specifying the relative quantities of total hydrogen and total oxygen present, either as the elementary substances or as constituents of the water; for then the proportions of the three substances adjust themselves so as to satisfy the conditions of the equilibrium between them, for example, so as to satisfy the mass-action law. The number of components in this case is therefore two.

The composition of a gaseous phase containing hydrogen, oxygen, and water-vapor at low temperatures where there is no reaction between the substances is evidently determined only when the relative quantities of hydrogen, oxygen, and water in the phase are specified. The number of components is therefore three under these conditions.

It is obvious from these examples that the number of components is determined not only by the substances present, but also by the equilibria that are established between them. It is therefore advisable to write chemical equations expressing all the equilibria actually established, so as to make sure that the proportion of every chemical substance present in any phase would be determined by specifying that definite relative quanti-

ties of the components adopted are present in that phase, and to make sure, on the other hand, that more components have not been adopted than are necessary.

Another aspect of the matter may be considered. In a gaseous phase where hydrogen, oxygen, and water are in chemical equilibrium, one particular system could be produced by taking water as the only component; but the phase considerations of this chapter have reference always to a series of systems of the same qualitative, but varying quantitative composition; and such a series containing hydrogen, oxygen, and water-vapor in every possible proportion cannot be produced out of water alone, but can be produced out of hydrogen and oxygen. These systems are therefore properly regarded as consisting of two components. As another example consider a gaseous phase containing HCl , O_2 , Cl_2 , and H_2O . By taking HCl and O_2 as two components, the other two substances can be produced out of them by the reaction $\text{O}_2 + 4\text{HCl} = 2\text{Cl}_2 + 2\text{H}_2\text{O}$, but only in equivalent proportions. To produce a system containing the four substances in any proportion whatsoever, it is necessary to make use of a third component, either Cl_2 or H_2O . Thus, either by adding Cl_2 to a mixture containing O_2 and HCl in any proportions and Cl_2 and H_2O in equivalent proportions, or by removing Cl_2 from such a mixture, any composition whatever can be secured. The systems are therefore said to consist of three components. It may be further noted that, though the number of components is fixed, there is a certain arbitrariness in their selection. Thus, although in this example O_2 , HCl , and Cl_2 have been used as the components, any other three of the four substances might be employed. It is, however, usual to select as components the simplest substances.

Determination of Components.

Prob. 3. — Specify the components which will produce phases containing the following chemical substances, assuming chemical equilibrium to be established between them. In answering this question, write chemical equations expressing all the equilibria that may be established between these substances, making sure that all the substances can be produced in any proportion from the specified components, and that all those components are necessary. *a.* Gaseous NH_3 , NO , O_2 , H_2O . *b.* Solution con-

taining H_2O , $(\text{H}_2\text{O})_2$, $\text{NaCl} \cdot 2\text{H}_2\text{O}$, NaCl , Na^+ , Cl^- . *c.* Solution containing H_2O , NH_4CN , NH_4^+ , CN^- , NH_3 , NH_4OH , HCN .

Prob. 4. — Specify the components of the systems that exist in the following groups of phases, assuming chemical equilibrium to be established between the substances named: *a.* Solid HgO , gaseous Hg and O_2 . *b.* Solid CaCO_3 , solid CaO , gaseous CO_2 . *c.* Solid $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, solid $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, solution of $\text{Mg}^{++}\text{SO}_4^-$ in water, water-vapor. *d.* Solid carbon; gaseous H_2O , H_2 , CO , and CO_2 . *e.* Solid iron, solid FeO , gaseous CO and CO_2 . *f.* Solid iron, solid FeO , solid carbon, gaseous CO and CO_2 .

3. Derivation of the Phase Rule from the Concept of Molar Free Energy. — In order to determine fully the state of one-phase systems consisting of any number C of components (as defined in the preceding article), evidently the chemical composition of the phase and in addition any external factors that determine its properties must be specified. The composition of the phase is fully determined by specifying the mol-fractions of all but one of the components, that is by specifying $C - 1$ quantities. The only external factors which commonly affect the properties of a phase of specified composition are temperature and pressure; but in special cases certain other factors, some of which are mentioned below, have an appreciable influence. Representing the number of such external determining factors by n , the variance or total number of the independent variables that must be specified is $C - 1 + n$. In any system, therefore, in which the number of phases P is one, the sum of the number of phases and the variance V is equal to $C + n$; that is, $P + V = C + n$; or, for the common case where pressure and temperature are the only external determining factors, $P + V = C + 2$. For example, the state of one-phase systems consisting of three components (1, 2, 3) is fully determined by specifying four quantities, namely, the mol-fractions (X_1 and X_2) of any two of the components and the pressure (p) and temperature (T); hence any intensive property whatever of the system, such as its density d , can be expressed as some function of these four variables, such as $d = f(X_1, X_2, p, T)$. In the general case, where the number of components is C and the number of external factors is n , the function becomes

$$d = f(X_1, X_2, \dots X_{C-1}, p, T, \dots).$$

other factors come into play. For example, this is sometimes true of intensity of illumination or of electric or magnetic field. Thus illumination of silver chloride increases its dissociation-pressure; and under certain conditions an electric discharge through an equilibrium mixture of nitric oxide, nitrogen, and oxygen increases the proportion of nitric oxide in the mixture. Another factor which makes the value of n greater than 2 is introduced when different pressures are applied by means of semi-permeable walls to different phases of the system. Thus the pressure of the vapor in equilibrium with a liquid is progressively increased (as shown in *IV*, 26) when the liquid is subjected to an increasing pressure by means of a piston permeable for the vapor only. A common case of this kind is that where the atmosphere acts as such a piston, exerting a pressure on the liquid and solid phases of the system, but not on the components in the vapor phase.

II. ONE-COMPONENT SYSTEMS.

4. Representation of the Equilibrium Conditions by Diagrams. — In the case of one-component systems the conditions under which the different phases exist in equilibrium with each other are fully represented by pressure-temperature diagrams; for the state of any phase of such systems is evidently determined when the pressure and temperature are specified. Thus the pressure-temperature diagram for the component water (Fig. 1; *I*, 18) represents the behavior of water at pressures less than 250 atm. for a temperature range, -2° to 400° . As shown by the lettering of the fields, there is only one solid phase, the common crystalline form of ice, which is capable of existence in this part of the water diagram.

FIGURE 1. PRESSURE-TEMPERATURE DIAGRAM FOR SULFUR.

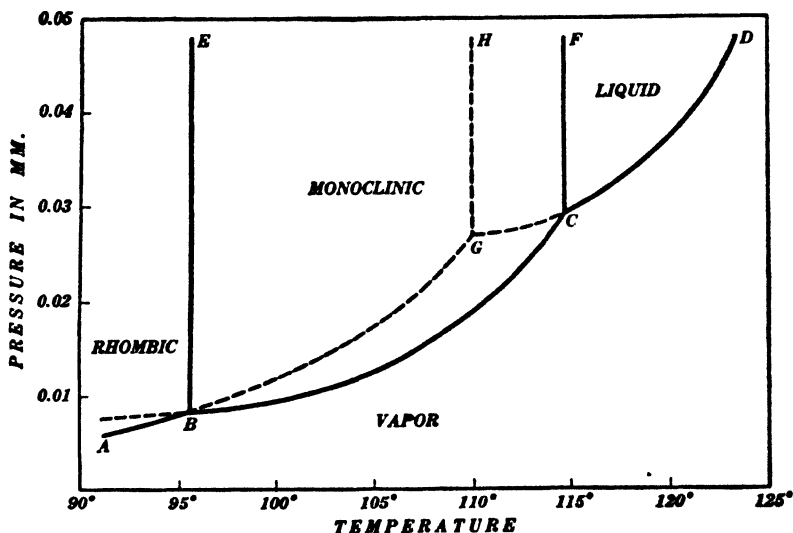


Figure 1 shows a part of the pressure-temperature diagram for the component sulfur, which forms not only liquid and gaseous phases, but also two solid phases, known from their crystalline forms as rhombic and monoclinic sulfur. In the diagram the (vapor-pressure) curve *AB* represents the pressures at which rhombic sulfur and sulfur-vapor are in equilibrium at various temperatures; the (vapor-pressure) curve *BC* represents

the pressures at which monoclinic sulfur and sulfur-vapor are in equilibrium at various temperatures; and the (transition-temperature) curve BE represents the temperatures at which monoclinic and rhombic sulfur are in equilibrium at various pressures. Temperatures, like these, at which two solid phases are in equilibrium with each other are called *transition-temperatures*.

The point of intersection B of these three curves shows the only temperature and pressure at which rhombic sulfur, monoclinic sulfur, and sulfur-vapor are in equilibrium with one another. A point, like this, at which three phases coexist is called a *triple point*.

The (vapor-pressure) curve CD represents the pressures at which liquid sulfur and sulfur-vapor are in equilibrium with each other at various temperatures; and the (melting-point) curve CF represents the temperatures at which monoclinic sulfur and liquid sulfur are in equilibrium at various pressures. The point C is evidently a second triple point at which monoclinic sulfur, liquid sulfur, and sulfur-vapor coexist. As indicated on the diagram, the fields between the different lines show the conditions under which sulfur exists as a single phase.

Prob. 5. — Behavior of Sulfur Derived from the Diagram. —

Describe with the aid of the diagram the changes that take place, *a.* when sulfur is heated in an evacuated tube in contact with its vapor from 90° to 125° ; *b.* when sulfur is allowed to cool from 125° to 90° , the pressure being kept constant at 0.04 mm.

The slope of any line on a pressure-temperature diagram of a one-component system is expressed by the Clapeyron equation (II, 31). Thus the slope of the melting-point curve of the common crystalline form of ice at 0° computed from its heat of fusion and the corresponding volume change (Prob. 77; II, 31) is negative and equal to 0.0075° per atmosphere. The lines BE and CF on the sulfur diagram can be similarly shown to have very small positive slopes of such magnitudes that the lines converge at higher pressures. The point of intersection determined experimentally is 154° and 1400 atm.

Unstable Forms.

Prob. 6. — a. To what equilibria do the curves BG , GC , and GH and the point G in the figure correspond? *b.* Considered with reference to these equilibria, to what form of sulfur do the

fields $EBGH$, $HGCF$, and GBC correspond? *c.* In what sense are these equilibria unstable?

Prob. 7. — Draw a sulfur diagram extending to pressures above the triple-point for rhombic, monoclinic, and liquid sulfur.

Prob. 8. — Find the free-energy decrease that attends the transition at 105° of 1S from the rhombic into the monoclinic form, each being at a pressure equal to its vapor-pressure, assuming that the molecular formula of the sulfur vapor is S_8 .

Prob. 9. — By comparing the free energy per gram of monoclinic sulfur with that of rhombic sulfur at 25° and 1 atm., show which of these forms has the greater solubility at 25° in any solvent, such as carbon bisulfide.

Prob. 10. — *Pressure-Temperature Diagram for Water at High Pressures.* — Investigation of the equilibrium conditions between phases in systems of water at high pressures (*Bridgeman, 1912*) shows the existence of several crystalline forms of ice, which have been designated by the numerals I, II, III, V, and VI. Construct from the following results of such investigations a pressure-temperature diagram, and letter the fields so as to show the stable form of water at any point.

<i>Phases at Equilibrium</i>	<i>Temperature</i>	<i>Pressure</i>
I, Liq. Vap.	$+ 0.0098^\circ$	0.00602 atm.
I, III, Liq.	$- 22^\circ$	2430 "
III, V, Liq.	$- 17^\circ$	3420 "
V, VI, Liq.	$+ 0.16^\circ$	6160 "
I, II, III	$- 34.7^\circ$	2100 "
II, III, V	$- 24.3^\circ$	3400 "
I, II	$- 80^\circ$	1700 "
II, V	$- 35^\circ$	4200 "
V, VI	$- 30^\circ$	6100 "
VI, Liq.	$+ 16^\circ$	8000 "

How great the likelihood is for a substance to remain in the same form after passing through a melting-temperature or transition-temperature and thus to exist in an unstable form depends in large measure on the nature of the substance. The following general statements in regard to it can, however, be made. A crystalline solid cannot as a rule be heated appreciably above its melting-point; thus, ice always melts sharply at 0° (under a pressure of 1 atm.). On the other hand, a liquid (like water) can ordinarily be cooled to a temperature considerably below the freezing-point if agitation and intimate contact with solid particles, especially with the stable solid phase, is avoided.

Still more pronounced is the tendency of solid substances to remain in the same form upon being heated or cooled through a transition-temperature; thus rhombic sulfur can be heated to its melting-point (110°), although this is about 15° higher than the transition-temperature (95.5°) at which it should go over into monoclinic sulfur; and monoclinic sulfur can be cooled to room temperature without going over into the rhombic form, provided this be done quickly and without agitation.

The rate at which an unstable phase goes over into the stable one tends to increase with the distance from the transition-temperature; but when the substance is below its transition-temperature this tendency may be more than compensated by the greatly reduced rate of reaction which a considerable lowering of temperature always produces; thus white phosphorus is an unstable form, but the rate at which it goes over into the stable red form at room temperature is so small that it may be preserved unchanged for years; similarly, diamond is an unstable form of carbon at room temperature, but it does not go over into graphite or amorphous carbon.

An effective means of causing an unstable form to go over into a stable one is to mix it intimately with the stable form. The transition may also be accelerated by moistening the mixture of the two forms with a solvent in which they are somewhat soluble. These facts are made use of in the determination of transition-temperatures. Thus the transition-temperature of sulfur has been determined by charging a bulb with a mixture of rhombic and monoclinic sulfur, filling it with carbon bisulfide and oil of turpentine, keeping it for an hour first at 95° and then at 96° , and noting whether the liquid rose or fell in the capillary stem attached to the bulb. The volume was found to decrease steadily at 95° (owing to the transition of the monoclinic into the rhombic form), and to increase steadily at 96° (owing to the reverse transition), showing that the transition-temperature lies between 95° and 96° .

Prob. 11. — Transition in Relation to Solubility. — a. Suggest an explanation of the catalytic action of the solvent in accelerating the transition of the sulfur. *b.* Outline a method by which the transition-temperature of sulfur could be determined by quantitative solubility measurements.

III. TWO-COMPONENT SYSTEMS.

5. Systems with Solid and Gaseous Phases. — The equilibrium of systems consisting of solid and gaseous phases at constant temperature has already been considered (*VII, 14*) from the mass-action viewpoint. Their equilibrium in relation to temperature and pressure will now be considered from the phase-rule viewpoint.

When a two-component system consists of three phases, the phase rule evidently shows that the specification of one of the determining factors (for example, the temperature) fixes the state of the system and therefore the values of the other factors (for example, of the pressure and of the composition of the liquid or the gaseous phase). The pressures at which the different groups of three phases exist in equilibrium at various temperatures can therefore be represented by lines on a diagram in which the pressure and temperature are the coordinates.

Dissociation-Pressure and Its Relation to Temperature.

Prob. 12. — Calcium carbonate dissociates at high temperatures into CaO and CO_2 . *a.* Show from the phase rule that CaCO_3 can be heated in CO_2 gas at a given pressure through a certain range of temperature without any decomposition taking place. *b.* Show also that there is one temperature, and only one, at which a mixture of CaCO_3 and CaO can be kept under CO_2 at the given pressure without any change occurring.

Prob. 13. — The dissociation-pressure of solid calcium carbonate

is	10	180	320	580	760	1000 mm.
at	600°	800°	840°	880°	896°	910°

a. Construct a pressure-temperature diagram for this two-component system, lettering the fields so as to show what phases coexist at different temperatures and pressures. *b.* State at what temperature the solid begins to dissociate when it is heated in air free from carbon dioxide. *c.* State at what temperature it would dissociate completely when heated in a covered crucible (so that there is equalization of the pressure, but no circulation of air into the crucible). *d.* In lime-burning state what temperature would have to be maintained in the kiln if there were no circulation of gases through it. *e.* State what temperature would have to be

maintained if the coal used as fuel were burned to carbon dioxide with the minimum quantity of air and the combustion-products were passed up through the kiln.

Prob. 14. — The dissociation pressure of silver oxide (*Benton and Drake, 1932*)

is	0.1	0.2	0.5	1.0	2.0 atm.
at	128°	144°	170°	190°	213°

a. If finely divided silver be heated in the air, what proportion of it will be finally converted into oxide when the temperature is 140°? when it is 150°? *b.* How could silver oxide be heated to 170° without any decomposition?

Prob. 15. — Describe a method by which pure oxygen can be prepared from the air with the aid of the reaction $2\text{BaO}_2(\text{s}) = 2\text{BaO}(\text{s}) + \text{O}_2(\text{g})$.

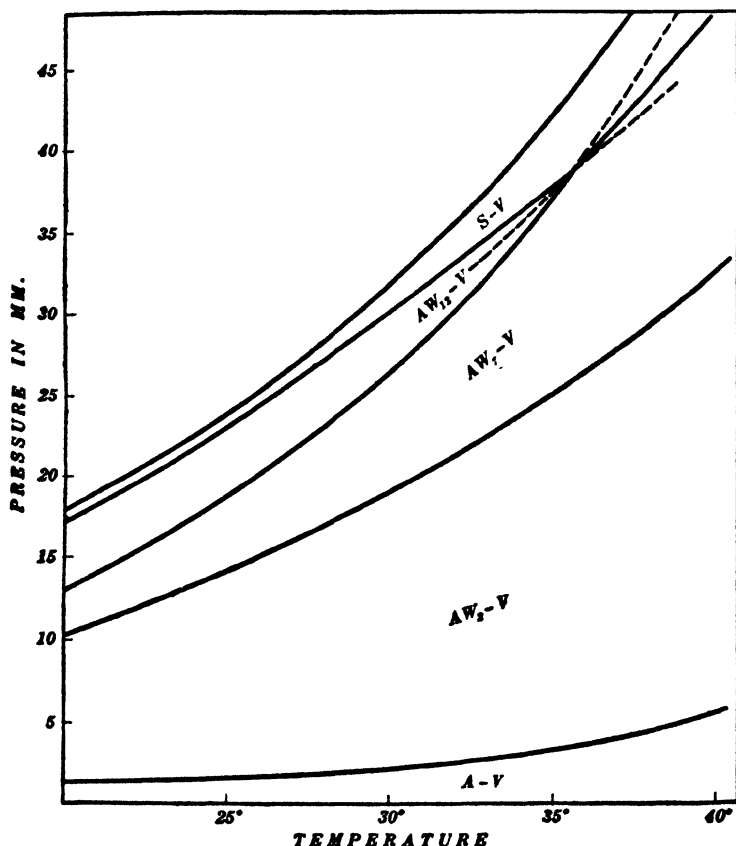
Prob. 16. — When a precipitate of hydrated manganese dioxide is ignited in the air it comes to a constant weight corresponding to the composition MnO_2 when the temperature is 450°, and to another constant weight corresponding to the composition Mn_2O_3 when the temperature is 500°; but when ignited in oxygen it changes to MnO_2 even at 500°. State what these facts show as to the dissociation-pressure of MnO_2 into Mn_2O_3 , and that of Mn_2O_3 into a lower oxide.

Prob. 17. — A method has been suggested for the standardization of sulfuric acid solutions which consists in adding an excess of ammonia solution, evaporating, drying the residue at 100°, and weighing it. In drying the salt some decomposition according to the reaction $(\text{NH}_4)_2\text{SO}_4(\text{s}) = \text{NH}_4\text{HSO}_4(\text{s}) + \text{NH}_3(\text{g})$ is likely to take place. How might the process be modified so as to hasten the drying and yet entirely prevent the decomposition?

6. Systems with Solid, Liquid, and Gaseous Phases. Pressure-Temperature Diagrams. — The two-component systems that involve salt-hydrates are of especial importance. The vapor-pressure relations of these substances at different temperatures may be represented by pressure-temperature diagrams, like that shown as Fig. 2. This diagram has reference to systems consisting of the two components disodium hydrogen phosphate (Na_2HPO_4) and water (H_2O), for the case that the vapor-phase (*V*), which consists only of water-vapor, is always present. These two components form the following solid phases: ice (*I*), anhydrous salt (*A*), dihydrate $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (*AW*),

heptahydrate $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ (AW_7), and dodecahydrate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (AW_{12}); also a solution-phase (S) of variable composition, approaching as one limit pure water, whose vapor-pressure is represented by the uppermost curve in the diagram.

FIGURE 2. VAPOR-PRESSURE—TEMPERATURE DIAGRAM FOR HYDRATES OF DISODIUM HYDROGEN PHOSPHATE.



The fields in Fig. 2 are lettered so as to show the different stable bivariant systems consisting of water vapor and of one other phase. The lines bounding the fields evidently represent the conditions of stable equilibrium for the corresponding univariant systems. Thus the lowest line shows for each tempera-

ture the pressure at which water vapor can exist in equilibrium with a mixture of the anhydrous salt and the dihydrate.

Prob. 18. — Interpretation of the Vapor-Pressure-Temperature Diagram for Salt-Hydrates. — At 30° one formula-weight of Na_2HPO_4 is placed in contact with a large volume of water-vapor at 1 mm., and the volume of the vapor is steadily diminished (so slowly that equilibrium is established) until finally there remains in contact with the vapor only the saturated solution (which contains the components in the ratio $1\text{Na}_2\text{HPO}_4 : 33.2\text{H}_2\text{O}$). State, with the aid of the figure, the changes that take place in the character of the other phases in contact with it, throughout the whole process.

Prob. 19. — Vapor-Pressure-Composition Diagram for Salt-Hydrates. — *a.* Plot the pressure of the vapor (as ordinates) against the number of formula-weights of water absorbed by the salt as abscissas for the process described in Prob. 18 (up to the point where 15 formula-weights have been absorbed). Mark the lines on the plot so as to show what phases are present during each stage of the process. *b.* Make a similar plot for the case that the process described in Prob. 18 takes place at 38° (instead of at 30°).

Prob. 20. — Experimental Determination of the Hydrates Formed by a Salt. — Describe an experimental method of determining what hydrates of copper sulfate exist at 25° .

Prob. 21. — Nonvariant Systems. — *a.* Predict the number of phases present in any nonvariant system of two components, and state the requirement of the phase rule in regard to the compositions of these phases. *b.* Designate the temperature, pressure, and nature of the phases present in the nonvariant system of disodium hydrogen phosphate and water shown in Fig. 2.

Prob. 22. — Transition-Temperature of Salt-Hydrates. — Describe with the aid of the figure what changes take place when a mixture of heptahydrate and dodecahydrate is heated from 30° to 38° in a sealed tube previously evacuated.

Prob. 23. — Conditions under which Salts are Efflorescent or Hygroscopic. — At 30° moist air is in contact with solid $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$. Under what conditions of humidity, *a.* would the salt remain unchanged? *b.* would it lose water? *c.* would it absorb water? (By the *humidity* of a gas is meant the ratio of the pressure of the water-vapor in the gas to the vapor-pressure of water at the same temperature.)

Prob. 24. — Drying of Hydrates without Decomposition. — *a.* State the conditions under which moist crystals of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ could be completely dried at 30° without danger of decomposition. *b.* Describe a method by which these conditions could be practically realized.

Separation of Hydrates from Solutions.

Prob. 25. — State what solid phase separates on evaporating a dilute solution of Na_2HPO_4 , *a.* at 30° , *b.* at 38° .

Prob. 26. — The equilibrium-pressures for the reaction $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) = CaSO_4 (anhydrite) + $2\text{H}_2\text{O}(\text{g})$ and the vapor-pressures of pure water at various temperatures are as follows:

Temperature	50°	55°	60°	65°
Gypsum	80	109	149	204 mm.
Water	92	118	149	188 mm.

The solubility of calcium sulfate is so small that the vapor-pressure of its saturated solution may be considered to be identical with that of water. *a.* State what happens on heating gypsum from 50° to 65° in a sealed tube previously evacuated. *b.* State what solid phase separates when a solution of calcium sulfate is evaporated at 55° , and at 65° . *c.* State what solid phase would separate upon evaporating the solution at 55° if, when it became saturated, enough calcium chloride were added to reduce its vapor-pressure by 10%. Give the reasons in each case.

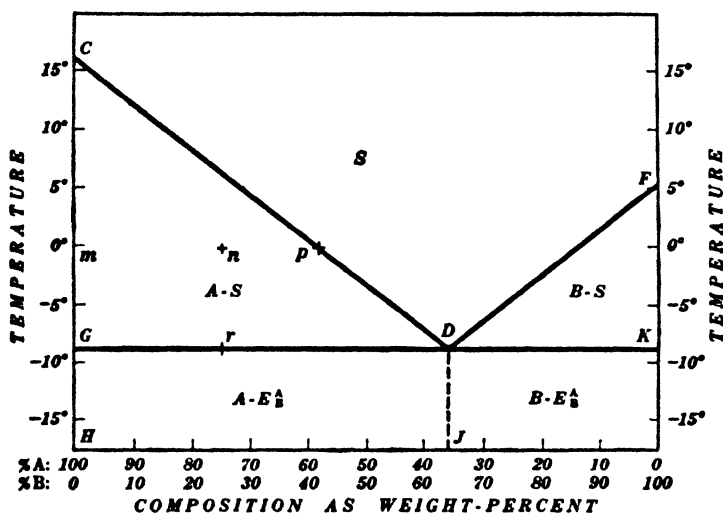
Prob. 27. — *Dehydration of Organic Liquids by Salts.* — When isoamyl alcohol ($\text{C}_5\text{H}_{11}\text{OH}$) and water are shaken together at 25° till equilibrium is attained, two liquid phases result, one containing 36.84 mol-percent, and the other 99.50 mol percent of water. The vapor-pressure of water at 25° is 19.1 mm. in a 20.5 mol-percent, 14.5 mm. in a 13.1 mol-percent, and 8.4 mm. in a 6.9 mol-percent solution of it in isoamyl alcohol. Determine from these data and Fig. 2 the extent to which the mol-percent of water in isoamyl alcohol can be reduced by shaking at 25° isoamyl alcohol saturated with water with a large excess of each of the following substances: *a.* $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; *b.* $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$; *c.* $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$; *d.* Na_2HPO_4 .

7. Systems with Solid and Liquid Phases. Temperature-Composition Diagrams. — In a two-component system the composition of a solution which coexists with its vapor and a solid phase is evidently fully determined by specification of the temperature, the system being univariant. The relation between this composition and the temperature can therefore be represented by a diagram in which these factors are plotted as coordinates.

It is evident that the equilibrium conditions of a two-component system can still be represented by a temperature-composition diagram when the specification that the vapor-phase

is present is replaced by the specification that the pressure has some definite value (greater than that at which the vapor can exist). Moreover, since pressure has only a small effect on equilibria in which solid and liquid phases are alone involved, the lines on the temperature-composition diagram have substantially the same position when the system is under a pressure of one atmosphere as they do when it is under the pressure of the vapor. And in practice composition-temperature diagrams are ordinarily constructed from data determined under the atmospheric pressure.

FIGURE 3. TEMPERATURE-COMPOSITION DIAGRAM FOR ACETIC ACID AND BENZENE.



The form of the temperature-composition diagram varies greatly with the character of the solid phases which the components are capable of producing. The simplest type of such a diagram is that in which the two components A and B do not form any solid compound with each other, but separate from the solution in the pure state. This type is illustrated by Fig. 3, which shows the complete diagram for systems composed of acetic acid (A) and benzene (B) at one atmosphere.

The freezing-point curve CD represents the composition of the solutions (S) which are in equilibrium with solid A, and

the freezing-point curve DF represents the composition of the solutions which are in equilibrium with solid B at different temperatures. The point D at which the solution is in equilibrium with the two phases A and B is called the *eutectic point*. When a solution in the condition corresponding to this point is cooled, it solidifies completely without change of composition or temperature to a mixture of the two solid phases A and B. This mixture is usually so fine-grained and intimate that it differs markedly in texture from ordinary mixtures of the same solid phases. It is called the *eutectic mixture*, or simply the *eutectic*.

Prob. 28. — Eutectics in Relation to the Phase Rule. — Show that the phase rule requires that a solution at the eutectic point solidify without change of temperature or composition when heat is withdrawn from it.

Prob. 29. — Effect of Cooling a Solution Predicted from the Diagram. — A tube containing a solution of 75% of benzene and 25% of acetic acid at 10° is placed within an air jacket surrounded by a freezing mixture at -20° , so that the system slowly loses heat, till its temperature falls to -10° . Predict with the aid of the figure the values of the temperature and composition of the solution at which any phase appears or disappears. State also the character of the solid mixture finally obtained.

Prob. 30. — Cooling Curves. — *a.* On a diagram having as ordinates the temperatures in degrees and as abscissas the time of cooling in arbitrary units draw curves representing in a general way the rate at which the temperature decreases when a solution of 75% of benzene and 25% acetic acid is cooled as described in Prob. 29, assuming, first, that the liquid undercools without the separation of any solid phase; and assuming, secondly, that the solid phases separate so that there is always equilibrium. Take into account the fact that on cooling a system there is always an evolution of heat whenever a new phase separates. *b.* Draw on the same diagram, at the right of these curves, a new cooling curve showing how the temperature changes when pure benzene is cooled from 10° to -10° . *c.* Draw a cooling curve also for the case that a solution of 64% of benzene and 36% of acetic acid is cooled from 10° to -10° .

The fields in the diagram also become of much significance, when the composition represented by the abscissas is understood to be that of the whole system — not merely that of the liquid phase. Thus, when the system consists of the sub-

stances in such a proportion (thus, 25% of B to 75% of A) and is at such a temperature (thus, 0°) that its condition is represented by a point n within the field CDG , the diagram shows that it consists of the two phases, solid A and solution S of the composition (corresponding to the point p) at which these two phases are in equilibrium at the given temperature. Similarly, when the system has a composition and temperature corresponding to any point within the field $G DJH$, it consists of solid A and the eutectic mixture E_B^A , which always has the composition corresponding to the point D . It can readily be shown, moreover, that, when the state of the system is represented by the point n , the weight of the solid A is to the weight of the solution present as the length of the line joining n and p is to the length of the line joining m and n ; and similarly, that at any point below r on the same ordinate with it the weight of pure A is to the weight of the eutectic mixture present as the length of the line rD is to that of the line Gr . It follows from the latter statement that, when equal weight samples of solutions of different composition are slowly cooled under the same conditions, the constant temperature time-interval during which A and B separate together as eutectic is greatest for a solution of the eutectic composition, and becomes diminishingly small as the composition of the (original) solution approaches that of either pure component. Furthermore, as indicated in the cooling curves of Fig. 4, the time taken for the solidification of a solution of the eutectic composition at the eutectic point is approximately equal to that taken for the solidification of an equal weight of either pure component at its freezing-point.

Prob. 31. — Nature of the Solid Phases. — How do the two rectangular fields at the bottom of the figure differ with respect to *a.* the phases present; *b.* the texture of the mixture?

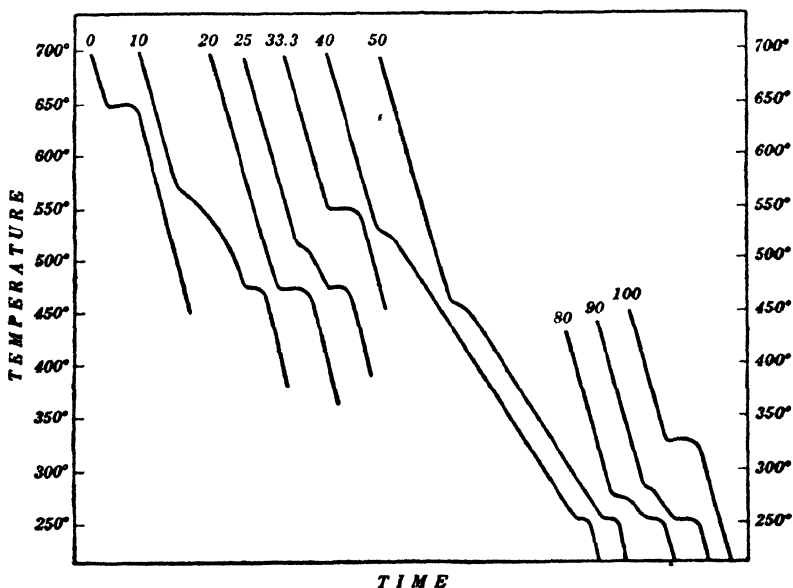
Prob. 32. — Relative Weights of the Separate Phases. — Derive the principle stated in the text in regard to the weight-ratio of solid separated to residual solution at any definite temperature during solidification.

Prob. 33. — Eutectic Composition and Temperature in Relation to the Laws of Freezing-Point Lowering. — Lead (which melts at 327°) and silver (which melts at 960°) form a eutectic which melts at 305° . The heat absorbed by the fusion of one atomic weight of lead is 1161 cal. Calculate the composition of the

eutectic, taking into account the facts that the first part of a freezing-point curve can be located with the aid of the laws of perfect solutions, and that the molecules of metallic elements in dilute metallic solutions are as a rule identical with their atoms. Compare the calculated composition of the eutectic with that (3.8 Ag to 94.2 Pb) derived from cooling curves.

Prob. 34. — Metallurgical Process of Enriching Lead-Silver Alloys Resulting from the Reduction of Ores. — A technical process of enriching lead-silver alloys has been based on the facts stated in Prob. 33. Describe how this process might be applied to a melt containing 1 at. wt. of silver and 99 at. wts. of lead, and state the extent to which the percentage of silver could be thereby increased.

FIGURE 4. COOLING CURVES FOR SYSTEMS OF MAGNESIUM AND LEAD.



The types of temperature-composition diagrams to be next considered are those for systems of which the components form one or more compounds which separate as solid phases. The simplest case, illustrated by Prob. 35, is that in which the solid compounds melt on heating. Another important case, illustrated by Prob. 36, is that in which a solid compound separates which, when heated, instead of melting, undergoes transition into another solid compound and a liquid phase.

The diagrams for such systems may be constructed either from cooling curves or from the results of solubility and freezing-point measurements. The former method is used in the case of alloys and other high-melting systems (as in Prob. 35); the latter, in the case of systems involving solutions at moderate temperatures (as in Prob. 36).

Prob. 35. — Construction of Temperature-Composition Diagrams from Cooling Curves. — Figure 4 shows the cooling curves for a series of mixtures of magnesium and lead containing the atomic percentages of lead shown by the numbers at the tops of the curves. On a diagram whose coordinates are temperature and atomic percentages plot points representing the temperature at which the solidification of each mixture begins and ends. Draw in solid lines representing the freezing-point curves. Draw also lines limiting the different fields (as was done in the benzene-acetic-acid diagram), and letter the fields so as to show of what the system consists in each field.

Construction of a Temperature-Composition Diagram for Salt Hydrates.

Prob. 36. — Construct a temperature-composition diagram for the system composed of Na_2HPO_4 and H_2O by plotting the following values of the weight-percentage (100 x) of Na_2HPO_4 in the saturated solution as abscissas against the temperature (t) as ordinates. The solid phase which is in equilibrium with the solution (S) at a pressure of 1 atm. is indicated by the letters above the data.

	<i>Ice</i>	<i>AW_{1s}</i>	<i>AW_{1s}</i>	<i>AW_{1s}</i>	<i>AW_{1s}</i>	<i>AW₇</i>
100 x	1.1	2.4	5.5	19.2	30.0	33.7
Temp.	− 0.5°	0°	15°	30°	35°	38°
	<i>AW₇</i>	<i>AW₇</i>	<i>AW_s</i>	<i>AW_s</i>	<i>AW_s</i>	
100 x	38.0	43.5	44.7	46.6	48.0	
Temp.	43°	48°	50°	55°	60°	

Draw in on the diagram lines representing the equilibrium conditions, and mark each line with letters indicating the phases which coexist under the conditions represented by the line; and at each triple point designate the phases that coexist there, the temperature, and the composition of the solution.

Prob. 37. — As a means of determining what the fields in the diagram signify with respect to the phases present, proceed as follows. *a.* State the solid phases that separate, and the way in which the composition of the residual solution changes, on cooling

from 55° to -5° at 1 atm. solutions containing 1% and 20% of Na_2HPO_4 . Draw in on the diagram lines bounding the fields within which the phases ice I and solution S coexist, within which AW_{12} and solution coexist, and within which ice and AW_{12} coexist; and letter the fields correspondingly. (Note that at any definite temperature the composition limits of any such field are the compositions of the two phases that are in equilibrium at that temperature, since these are the limiting compositions of mixtures that can be made up of these two phases.) *b.* From a similar consideration deduce and state the results of cooling from 55° to -5° solutions containing 36% and 42% of Na_2HPO_4 . Draw in on the diagram lines bounding the fields within which the phases AW_7 and solution S coexist, and within which the phases AW_{12} and AW_7 coexist. (Note that, when the triple point is reached, the phase AW_{12} separates, thereby tending to decrease further the percentage of Na_2HPO_4 in the solution but, since the composition must remain constant so long as three phases are present, the phase AW_7 re-dissolves; and this process continues as heat is withdrawn either till the phase AW_7 is consumed or till the solution dries up.) *c.* Finally state the results of cooling from 55° to -5° a solution containing 46% of Na_2HPO_4 . Draw in on the diagram lines bounding the fields within which the phases AW_2 and solution S coexist, and within which the phases AW_7 and AW_2 coexist.

Prob. 38. — Preparation of Different Hydrates by Evaporation at Different Temperatures. — Determine from the diagram within what limits of temperature a solution of Na_2HPO_4 must be evaporated in order to obtain in the pure state, *a.* $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; *b.* $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$; *c.* $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$. (The conditions under which such salt-hydrates can be dried without change in composition were considered in Prob. 24.)

Conditions of Unstable Equilibrium.

Prob. 39. — a. By extending by dotted lines the appropriate curves on the diagram, determine the solubilities, in terms of the percentage of anhydrous salt in the solution, of AW_7 at 45° and 50° , and of AW_2 at 45° and 50° . *b.* Prove that in contact with the solution AW_7 is unstable at 50° with respect to AW_2 by showing with the aid of these solubility values what happens when AW_7 is placed in contact with a solution saturated at 50° with respect to AW_2 . *c.* Show that at 45° the more soluble hydrate is again the unstable one in contact with the solution.

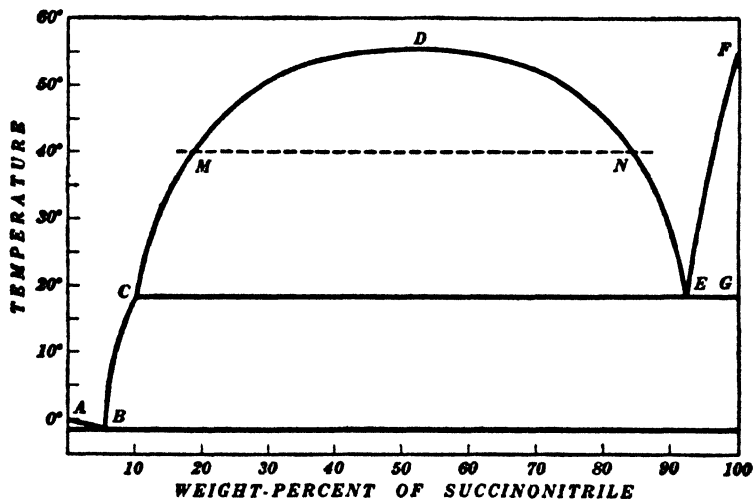
Prob. 40. — By extending the appropriate curves on the diagram predict, *a.* at what temperature salt would begin to separate on cooling a 30% Na_2HPO_4 solution in case the stable hydrate AW_{12} separates, and in case the solution remains super-

saturated with respect to this hydrate; *b.* at what temperature the hydrate AW_{12} would melt if on heating its transition into AW_7 and solution did not take place.

Prob. 41. — Correlation of Vapor-Pressure-Temperature and Temperature-Composition Diagrams. — With the aid of the diagram under consideration and Fig. 2 (VIII, 6) determine and tabulate for the temperatures 20, 25, 30, 35.5 and 40° the vapor-pressures and percentage compositions of the saturated solutions and the nature of the solid phases with respect to which the solutions are saturated. (Note that the effect of pressure on the solubility is here neglected.)

Brief consideration may also be given to systems involving two liquid phases as well as solid phases. Such systems are occasionally met with among alloys, and frequently among non-metallic substances, such as bromine and water, or isoamyl alcohol and water, which are partially miscible with each other.

FIGURE 5. TEMPERATURE-COMPOSITION DIAGRAM FOR WATER AND SUCCINONITRILE.



Their relations are illustrated by Fig. 5. In this diagram the curves *CD* and *DE* represent the compositions of the two liquid phases which are in equilibrium with each other. Thus, the points *M* and *N* show the limits of miscibility at 40° of the two liquid components. The curves *BC* and *EF* represent the compositions of solutions in equilibrium with solid succinonitrile.

Prob. 42. — Interpretation of Diagrams for Systems with Solid Phases and Two Liquid Phases. — a. With the aid of Fig. 5 state all that would happen on cooling from 60° to -10° systems containing 20, 80, and 95 percents of succinonitrile. *b.* State what would happen on gradually adding succinonitrile to 100 g. of water at 10° , at 40° , and at 60° . *c.* Letter each field so as to show of what phases the system consists at any point on the diagram.

8. Systems of Liquid and Gaseous Phases. — Systems of two components having a gaseous phase and a liquid phase (or two liquid phases when the components are incompletely miscible in the liquid state) have already been discussed with reference to deviations from Raoult's law. The vapor-pressure-composition diagrams there considered (IV, 34) may now be treated as pressure-composition diagrams at constant temperature by lettering the fields so as to show the phases in which the system under consideration exists when its pressure and composition are represented by any point. The commonly occurring types of such diagrams are considered in the following problem.

Prob. 43. — Pressure-Composition Diagrams at Constant Temperature. — By reference to the vapor-pressure-composition diagrams shown in Fig. 7 (IV, 34) as *B*, *C*, *E*, and *F*, sketch four pressure-composition diagrams at constant temperature, which are typical of the following cases: (1) the vapor-pressure curve passes through neither a maximum nor a minimum value; (2) it passes through a maximum; (3) it passes through a minimum; and (4) the two components are incompletely miscible in the liquid state. Letter each field so as to show of what the system consists at any point.

The boiling-point diagram of any binary system at a definite pressure p may be readily constructed from a series of corresponding vapor-pressure-composition diagrams at different temperatures. The diagrams may then be interpreted as temperature-composition diagrams at constant pressure by lettering the fields to indicate the phases in which the system at the pressure p exists when its temperature and composition are represented by any point. The interrelation of vapor-pressure-composition and boiling-point-composition diagrams is illustrated by the following problems.

Prob. 44. — Temperature-Composition Diagram for Ideal Solutions.

The vapor pressure at	80°	83°	86°	89°	92°
of a pure liquid A is	560,	610,	665,	725,	790 mm.
and of a pure liquid B is	400,	435,	475,	520,	570 mm.

a. With the aid of these data and Raoult's law, draw on a large-scale vapor-pressure-composition diagram for each temperature two lines — one representing the total vapor-pressure of any solution of A and B; and the other representing the partial vapor-pressure of A above any solution. *b.* Determine from the plot the composition of the liquid which at 570 mm. boils at each of these temperatures; also the composition of the vapor which is in equilibrium with each of these solutions at its boiling-point. Determine also the boiling-point of pure liquid A at 570 mm., and tabulate all of these results. *c.* Construct from these results a large-scale temperature-composition diagram at 570 mm., and letter each field so as to show of what the system consists at any point.

Prob. 45. — Temperature-Composition Diagrams for Non-Ideal Solutions. — In correspondence to the pressure-composition diagrams (at constant temperature) considered in Prob. 43, sketch four temperature-composition diagrams at constant pressure, which are typical of the following cases: (1) the boiling-point curve passes through neither a minimum nor a maximum; (2) it passes through a minimum; (3) it passes through a maximum; and (4) the two components are incompletely miscible in the liquid state. Letter each field so as to show of what the system consists at any point.

Pressure-composition and temperature-composition diagrams of the kind here considered find practical application in predicting the results of fractional-distillation at constant temperature (Prob. 54; *IV*, 34), and at constant pressure, as illustrated by Probs. 46, 47, 48. Similarly the results of fractional condensation of gaseous mixtures, illustrated by Prob. 49, can be predicted by reference to such diagrams.

Fractional Distillation at Constant Pressure.

Prob. 46. — A solution of 100 mols of each of the liquids of Prob. 44 is distilled at 570 mm. until its boiling-point rises 0.5°. *a.* Find from the diagram of Prob. 44*c* the molal compositions of the first and last portions of the distillate. *b.* Regarding the composition of the whole distillate as the mean of that of its first

and last portions (which is approximately true when only a small fraction of the liquid distills over), calculate the number of mols of A and B in the distillate and in the residue. *c.* The distillation of the residue is continued till its boiling-point rises 0.5° more. Calculate as in *b* the number of mols of A and B in this second distillate and in the residue. *d.* Tabulate the number of mols of A and B in the original liquid, the first distillate, the second distillate, and the final residue; the mol-fraction of A in each of these liquids; and the boiling-point of each of them. *Ans.* *b.* 52 mols of A, and 63 mols of B in the residue.

Prob. 47. — *a.* The first distillate obtained in *Prob. 46a* is redistilled until the residue attains the composition of the second distillate obtained in *Prob. 46c*. Find the mol-fraction of A in the new distillate and its boiling-point. *b.* The residue is now mixed with the second distillate obtained in *Prob. 46c*, and the distillation is continued till the residue has the composition of the residue obtained in *Prob. 46c*. Find the mol-fraction of A in the distillate thus obtained and its boiling-point. *c.* Tabulate the composition and the boiling-point of the original equimolar solution and of the three fractions into which it has now been resolved.

Note. — By repeated fractional distillation the two components of an ideal solution can be completely separated from each other, with the more volatile component in the final distillate and the less volatile in the residue.

Prob. 48. — At 1 atm. pure nitric acid has a boiling-point of 86° . A solution of nitric acid and water of the composition $\text{HNO}_3 \cdot 1.6\text{H}_2\text{O}$ distills at 1 atm. at a constant temperature of 121° . *a.* Sketch a temperature-composition diagram for predicting the general behavior of different solutions of nitric acid in water when subjected to fractional distillation at 1 atm. *b.* State what products would finally result as distillate and residue from the fractionation of solutions of the following compositions: $\text{HNO}_3 \cdot \text{H}_2\text{O}$; $\text{HNO}_3 \cdot 1.6\text{H}_2\text{O}$; and $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$.

Prob. 49. — Upon partial distillation at constant pressure a solution of two components A and B containing 20% of A, having a boiling-point of 80° , yields a residue containing 15% of A; and a mixture containing 75% of A, having a boiling-point of 60° , yields a distillate containing 70% of A. Construct a rough temperature-composition diagram for this two component system, and predict what products would finally result as distillate and residue from the fractionation of the 20% and of the 75% solution.

Prob. 50. — *Partial Condensation of Gaseous Mixtures.* — A gaseous mixture of normal pentane and butane containing 25 mol percent of pentane was partially condensed by passing it slowly through an open spiral tube maintained at 10° , the residual gas escaping at 1 atm. At 10° the vapor-pressure of pentane is 280

mm., and that of butane is 1300 mm. *a.* Make a pressure-composition diagram for systems of pentane and butane at 10° . *b.* Find, by reference to the diagram, the molal composition of the effluent gas and that of the condensate. *c.* Calculate the ratio of the weight of condensate to that of effluent gas. *d.* Determine from the diagram what gaseous mixtures cooled to 10° at 1 atm. would (1) be completely condensed, and (2) remain completely gaseous.

9. Systems Involving Solid Solutions. — The components sometimes separate from a liquid solution in the form of solid solutions, instead of in the form of the pure solid substances or of solid compounds of them. By *solid solutions* are meant physically homogeneous solid mixtures of two or more substances, that is, solid mixtures which contain no larger aggregates than the molecules of the substances.

In their equilibrium relations solid solutions closely resemble liquid solutions; differing from them mainly in the respect that the equilibrium conditions are less readily established, owing to the restricted molecular motion characteristic of the solid state. It is often true in solid systems that equilibrium is not established and that the solid phases fail to attain the uniform composition corresponding to equilibrium, unless the systems are kept for a time at a high temperature or at a temperature not far below the melting-point, where the molecules still retain sufficient mobility. The purpose of the process of *tempering* or *annealing* solid substances is to allow time for the establishment of equilibrium at temperatures so high that it may be rapidly attained.

In solid solutions in which equilibrium is really attained, each component lowers, as in liquid solutions, the vapor-pressure, solution-tendency, and mass-action or activity of the other component. As a result of these effects the freezing-point of a substance may be either raised or lowered by the addition of another substance, according as the solid solution which separates is more or less concentrated than the liquid solution, as is shown by the following problem.

Prob. 51. — Raising of Freezing-Point by Solutes. — The addition of benzene to thiophene raises the freezing-point of the thiophene, owing to the formation of solid solutions. *a.* Show

how this can be accounted for by sketching a diagram, similar to Fig. 3 (IV, 18), representing the logarithms of the vapor-pressure of thiophene in the pure liquid and solid states and in a liquid solution of benzene in thiophene, and draw in on the sketch a line showing the logarithm of the vapor-pressure of thiophene at various temperatures in a solid solution of benzene and thiophene of the composition of that which separates from the liquid solution. *b.* Show that the mol-fraction of benzene must be greater in the solid solution than in the liquid solution in order that the freezing-point may be raised, provided Raoult's law holds for the solid solution as usually seems to be approximately true when the proportion of solute is small.

The two components are sometimes soluble in each other in the solid state in all proportions, forming a complete series of solid solutions. In most cases, however, each component has only a limited solubility in the other solid, so that two series of solid solutions result, each covering only a limited range of composition.

The temperature-composition diagrams representing the equilibrium conditions between solid solutions and liquid solutions correspond completely with those for liquid solutions and their vapors, since in both cases there are involved two phases of variable composition. Thus systems in which there are solid solutions containing the components in all proportions may have diagrams of any of the first three types considered in Prob. 45; two of which are illustrated by Probs. 52 and 53. Systems in which the components have only partial miscibility in the solid state have a diagram of the fourth type in Prob. 45. Such systems are illustrated by Prob. 54, the diagram of which represents also certain other effects which have been already considered.

Alloys with Complete Series of Solid Solutions.

Prob. 52.—The cooling curves show that on cooling molten mixtures of nickel and copper solidification begins and becomes complete at the following temperatures, a solid solution separating in each case:

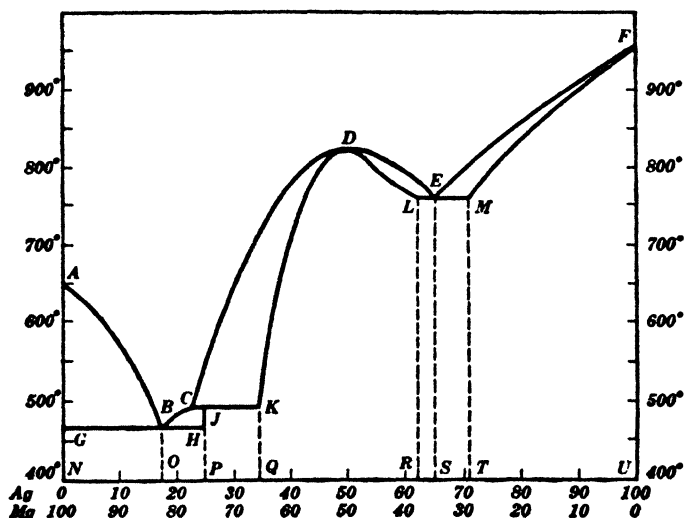
Percentage of nickel	0	10	40	70	100
Solidification begins	1083°	1140°	1270°	1375°	1452°
Solidification ends	1083°	1100°	1185°	1310°	1452°

a. Draw on a temperature-composition diagram two continuous curves corresponding to these data. Letter each field so as to show of what the system consists at any point. b. State what happens on slowly cooling a 50% mixture from 1400° to 1200° , giving the compositions of the liquid and solid solutions in equilibrium with each other at the temperatures at which solidification begins and ends, and at 1275° . (Note that the compositions of the liquid and solid solutions at any temperature are given by the points corresponding to that temperature on the upper and lower curves, since at any temperature the composition of the liquid phase is identical with that of a system from which at that temperature solid just begins to separate, and the composition of the solid phase is identical with that of a system which at that temperature just completely solidifies.)

Prob. 53. — Gold and copper form a complete series of solid solutions. The mixture containing 60 atomic percent gold has a constant melting-point of 880° . Gold melts at 1063° , and copper at 1083° . Sketch the temperature-composition diagram.

Prob. 54. — *Alloys Forming Compounds and Limited Series of Solid Solutions.* — In Fig. 6, constituting the diagram

FIGURE 6. TEMPERATURE-COMPOSITION DIAGRAM FOR SILVER AND MAGNESIUM.



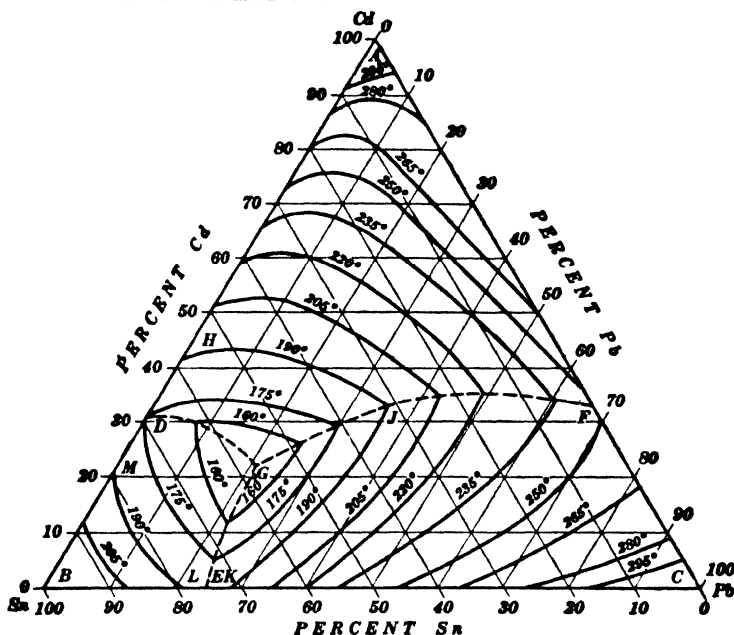
for silver-magnesium alloys, in which the composition is expressed in atomic percentages, the curves KD , DL , and MF represent the composition of solid solutions in equilibrium with the liquid

solutions whose composition is represented by the curves CD , DE , and EF , respectively. *a.* State what equilibria are represented by the curves AB and BC . *b.* State what compounds are indicated by the diagram. *c.* — *i.* State what happens on cooling slowly till complete solidification results a liquid mixture containing the following atomic percentages of silver: *c*, 90; *d*, 65; *e*, 55; *f*, 50; *g*, 30; *h*, 25; *i*, 20. *j.* Specify the phases in which the system exists when its composition and temperature are represented by any point in each of the fields, and letter the fields accordingly.

IV. THREE-COMPONENT SYSTEMS.

10. Systems with Liquid and Solid Phases. Temperature-Composition Diagrams. — In systems of three components existing in one solid phase and one liquid phase the composition is not determined by specification of the pressure and temperature, but becomes definite when the percentage or mol-fraction of one of the components is also specified. With such systems there must therefore be employed diagrams which show how the percentages or mol-fractions of the three components are related to one another. The most common form of diagram, one which

FIGURE 7. TEMPERATURE-COMPOSITION DIAGRAM FOR TIN, LEAD, AND CADMIUM.



has the advantage of treating the three components symmetrically, is an equilateral triangle, along the three sides of which are plotted the atomic percentages or mol-fractions of the three components, as in Fig. 7. In such a diagram the vertices then represent the pure components, points on the sides represent mixtures of each pair of components, and points within the

triangle represent mixtures of all three components. Thus the upper vertex would represent pure cadmium; the point *H*, a mixture consisting of 42% of Cd and 58% of Sn; and the point *G*, a mixture consisting of 22% of Cd, 57% of Sn, and 21% of Pb.

At any one temperature the various compositions of the liquid phase with which any definite solid phase is in equilibrium are represented on such a diagram by a line. Thus the lines *HJ*, *JK*, and *LM* represent at 190° the compositions of the liquid with which solid cadmium, solid lead and solid tin, respectively, are in equilibrium. The point *J* then evidently represents the composition of the liquid with which the two solid phases Cd and Pb are in equilibrium at 190°. Similar lines can be drawn corresponding to various other temperatures, thus giving a series of isotherms representing the effect of temperature on the equilibrium of the phases. The dotted line *FG* evidently shows the variation with the temperature of the composition of the liquid phase in equilibrium with the two solid phases Cd and Pb; the line *DG* shows the same thing for the two solid phases Cd and Sn; and the line *EG* for the two solid phases Sn and Pb. And the point *G* shows the only temperature and liquid composition at which the three solid phases Cd, Pb, and Sn coexist in equilibrium with the liquid phase. The mixture of three solid phases separating at this point is called the *ternary eutectic*, and the point itself the *ternary eutectic point*.

A more complete representation of the effect of temperature is secured by plotting temperatures along an axis perpendicular to the plane of the composition triangle. A model in the form of a triangular prism thus results, whose horizontal sections are the isotherms represented in a plane triangular diagram, like that in the figure.

Prob. 55. — Behavior of a Liquid Ternary Alloy on Cooling Predicted from its Temperature-Composition Diagram. — A completely liquid mixture of 50 Cd, 30 Sn, and 20 Pb is cooled till it wholly solidifies. *a.* State the temperature at which solidification begins and the nature of the solid phase which then separates. *b.* State the direction on the diagram which on further cooling the changing composition of the liquid phase follows. (Note that the separation of the solid phase does not change the ratio of the atomic quantities of the other two components in the liquid phase.) *c.* State the temperature at which a second solid phase

begins to separate, the composition of the liquid phase, and the nature of the solid phase. *d.* Describe what happens on further cooling. *e.* Describe the texture of the solid alloy.

11. Systems with Gaseous, Liquid, and Solid Phases in Relation to the Phase Rule and Mass-Action Law. — Three-component systems existing in gaseous, liquid, and solid phases will be here considered only with reference to the phase rule, and incidentally to the mass-action law in order to show the relations between these two principles.

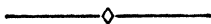
Applications of the Phase Rule and Mass-Action Law.

Prob. 56. — *a.* Show by the equilibrium laws applicable to dilute solutions how the solubility of CaCO_3 in water saturated with CO_2 gas at a given temperature is quantitatively related to the pressure of the CO_2 gas, considering that the salt in the solution is substantially all $\text{Ca}^{++}(\text{HCO}_3^-)_2$. *b.* Show that the phase rule requires that the solubility of CaCO_3 in water saturated with CO_2 gas is definitely determined when the pressure and temperature are specified.

Prob. 57. — Silver chloride forms with ammonia two solid compounds $\text{AgCl} \cdot 1\frac{1}{2}\text{NH}_3$ and $\text{AgCl} \cdot 3\text{NH}_3$, which exist in contact with aqueous solutions. Determine by the phase rule the variance of systems in which the following phases are present, and illustrate what this variance signifies by specifying in each case factors that would determine the state of the system: *a.* solid AgCl , aqueous NH_3 solution, vapor; *b.* solid AgCl , solid $\text{AgCl} \cdot 1\frac{1}{2}\text{NH}_3$, solution, vapor; *c.* solid AgCl , solid $\text{AgCl} \cdot 1\frac{1}{2}\text{NH}_3$, solid $\text{AgCl} \cdot 3\text{NH}_3$, solution, vapor. *d.* At 25° ammonia vapor is in equilibrium with the solids AgCl and $\text{AgCl} \cdot 1\frac{1}{2}\text{NH}_3$ at 10 mm. and with the solids $\text{AgCl} \cdot 1\frac{1}{2}\text{NH}_3$ and $\text{AgCl} \cdot 3\text{NH}_3$ at 105 mm. State under what conditions each of these two pairs of solid phases would exist in equilibrium with an aqueous solution. *e.* With the aid of the data of Prob. 37 (IV, 28), determine the concentration of free NH_3 in the aqueous solution at which AgCl is converted into $\text{AgCl} \cdot 1\frac{1}{2}\text{NH}_3$ at 25° . *f.* Assuming that the AgCl in the solution is substantially all in the form of completely ionized $\text{Ag}(\text{NH}_3)_2^+\text{Cl}^-$, derive from the equilibrium laws of dilute solutions a relation between the solubility s of AgCl and the partial pressure p of NH_3 in the vapor, first, when the solid phase is AgCl , and secondly, when it is $\text{AgCl} \cdot 1\frac{1}{2}\text{NH}_3$.

The preceding problems illustrate the characteristic differences between the conclusions to be drawn from the phase

rule and from the mass-action law. The phase rule is qualitative, its application presupposes no special knowledge beyond that of the number of components and phases, and it is applicable without any limitation of concentration. The mass-action law is quantitative, its application presupposes knowledge of the molecular species present, and, if numerical values are to be computed, also of their dissociation-constants. Furthermore, quantitative application of the mass-action law in its exact form presupposes knowledge of the activity-coefficients of the molecular species involved in the equilibrium.



CHAPTER IX

SYSTEMIZATION OF FREE ENERGY VALUES

I. FREE ENERGY OF CHEMICAL CHANGES FROM EQUILIBRIUM MEASUREMENTS.

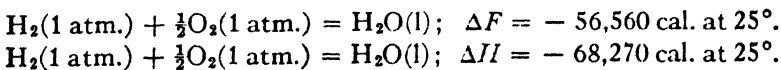
1. General Plan of Systemizing Free Energy Values. —

Since a knowledge of the changes in free energy attending chemical changes makes it possible to predict the direction in which they can take place and the conditions under which they are in equilibrium, the working out of a complete system of free energy values becomes an experimental problem of great chemical importance. The more general principles by which changes in free energy can be determined by equilibrium measurements have already been fully considered in the preceding chapters. There will now be presented a systemization of the molar free energies of substances which is based on these principles coupled with certain conventions. These conventions have also been already considered, but will here be reviewed and discussed in relation to the proposed systemization.

The molar free energy of a substance (*IV*, 40) is a quantity which, like its molar heat-content, is fully determined by its state. Free energy values will be expressed in calories on account of their close relations with heat-content data, which are commonly so expressed. However, in order to assign a definite value to either the molar free energy or molar heat-content of a substance in a definite state, it is necessary to adopt some arbitrarily chosen zero point in the free energy or the heat-content scale. The same zero point is chosen (*II*, 11 and *IV*, 43) for the two scales. Namely, the molar free energy (or molar heat-content) of a substance in any definite state at any definite temperature is considered to be equal to the free energy (or heat-content) increase that attends the formation of one mol of the substance in that state out of the pure elementary substances at the same temperature, and at a pressure of one atmosphere, each elementary substance being in the state of aggregation that is the stable one at this temperature and pressure. Stated more ex-

actly, and in a different way, the molar free energy (or heat-content) at any definite temperature of each pure elementary substance in its most stable standard state of unit-activity (or fugacity) at that temperature (*IV*, 44) is considered to be zero; and the molar free energy (or heat-content) of any substance in any definite state at the same temperature is evaluated on this basis.

Changes in free energy and in heat-content are, as previously shown (*II*, 10 and *IV*, 43), conveniently represented by equations. For example, the free energy increase ΔF and the heat-content increase ΔH which attend at 25° and 1 atm. the formation of $\text{H}_2\text{O}(\text{l})$ out of $\text{H}_2(\text{g})$ and $\frac{1}{2}\text{O}_2(\text{g})$ are shown by the equations:



The equation describes the change in state to which the values ΔF and ΔH apply at 25°. By considering the chemical formulas in the equations to represent numerical values of the molar free energies, or molar heat-contents, of the substances involved in the change in state, either of the above equations can be written as a completely balanced algebraic equation by subtracting ΔF or ΔH from the right hand member. Free energy calculations, like thermochemical calculations, are much simplified through the use of such equations.

When, as in the case just cited, the initial and final states of the substances involved are the conventional standard states of unit-activity (or fugacity), the corresponding values of the increase in free energy and in heat-content are designated by the symbols ΔF° and ΔH° , and called the standard free energy, and standard heat of the reaction, respectively. It has already been shown (*IV*, 46) that, for any such standard change in state, $-\Delta F^\circ = RT \ln K$, where K is the equilibrium constant characteristic of the change at the temperature T .

The partial molar free energy (or partial molar heat-content) of a substance in the dissolved state (*IV*, 40) is equal to the free energy (or heat-content) increase attending the formation of one mol of the pure substance out of the elementary substances plus that attending the introduction of it into an infinite quantity of the solution under consideration. The state of a substance in solution is commonly described by attaching

to the chemical formula a parenthesis showing the concentration or composition of the solution; for example $1\text{KCl}(\text{at } 0.1 \text{ wf.})$, $1\text{H}_2\text{SO}_4(\text{in } \text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O})$. The free energy of water (as solvent) in a solution, like its heat-content (*II, II*), is often conveniently referred to that of pure water (instead of to that of hydrogen and oxygen) as zero; and when so referred the symbol *Aq* (instead of H_2O) is used to describe its state; for example 5 Aq (in $\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

The partial molar free energy (or heat-content) of an ion, for example Pb^{++} , in aqueous solution is conveniently defined, in correspondence with the definition of electrode potentials (*V, 32*), as the increase in free energy (or heat-content) that attends the formation of one mol of the ion in a solution at the specified concentration out of the pure elementary substance in its most stable standard state, an equivalent quantity of hydrogen gas in its standard state (1 atm.) being formed at the same time out of hydrogen-ion in its standard state (1 *wm.*). Thus the free energy (or heat-content) of 1 Pb^{++} (in 0.1 *wf.* $\text{Pb}(\text{NO}_3)_2$) is equal to the free energy (or heat-content) increase attending the reaction, $\text{Pb}(\text{s}) + 2\text{H}^+(\text{ss. } 1 \text{ } \text{wm.}) = \text{Pb}^{++}(\text{in } 0.1 \text{ } \text{wf. } \text{Pb}(\text{NO}_3)_2) + \text{H}_2(\text{ss. } 1 \text{ atm.})$ —the standard molar free energy (or heat-content) of hydrogen-ion as well as that of the hydrogen gas being thereby arbitrarily assumed to be zero.

The proposed systemization of free energy (or heat-content) values may now be stated more definitely. It consists in compiling a systematic set of such relative values of the molar free energy and heat-content of substances in their several standard states of unit-activity at some definite temperature, for example at 25° .

2. Determination of Molar Free Energies from Equilibrium Measurements. — The various kinds of equilibrium measurements employed in the experimental determination of the molar free energies of substances in their different standard states are illustrated by the following problems.

*Free Energies of Elementary Substances in
Different Standard States.*

Prob. 1. — At 25° the vapor-pressure of pure iodine I_2 is 0.305 mm., its solubility in water is 0.00132 volume-molal, and

its distribution-ratio between carbon tetrachloride and water is 86, the equilibrium concentrations being expressed as volume-molalities. With the aid of these data, calculate the molar free energy of iodine at 25° in each of the following (hypothetical) standard states: *a.* $I_2(g)$ at 1 atm.; *b.* $I_2(1 \text{ vm. in } H_2O)$; and *c.* $I_2(1 \text{ vm. in } CCl_4)$.

Prob. 2. — At 25° the solubility in benzene of monoclinic sulfur is 23.2 g. and that of rhombic sulfur is 18.2 g. per liter of benzene. The molecular formula of sulfur in benzene has been shown by molecular weight determinations to be S_8 . Find the standard free energy of one atomic weight of monoclinic sulfur.

Prob. 3. — *Free Energy of Solutes at High Concentrations.* — *a.* Calculate the free energy of $1NH_3$ in a 8.6 vn. solution in water at 25° from the following data at 25°. The standard free energy of $1NH_3(g)$ is - 3910 cal. The vapor-pressure of NH_3 from a 0.2 vn. solution in water is 2.70 mm. The distribution-ratio of NH_3 between CCl_4 and H_2O is 0.0040 when the NH_3 is 0.2 vn. in the water, and 0.0086 when the NH_3 is 8.6 vn. in the water. *b.* State the principles involved. *c.* State how the same free energy might be obtained from another kind of measurement with the 8.6 vn. aqueous solution.

Free Energies Derived from Electromotive Forces.

Prob. 4. — Calculate the standard free energy of $1HCl(g)$ at 25° from the facts that at 25° the cell $H_2(1 \text{ atm.}), HCl(4 \text{ wf.}), Cl_2(1 \text{ atm.})$ has an electromotive force of 1.262 volts, and that the vapor-pressure of the HCl in its 4 formal solution is 0.0182 mm. *Ans.* - 22,790 cal.

Prob. 5. — *a.* Calculate the standard free energy of $1AgCl(s)$ at 25° from the combined electromotive force data of Prob. 4 (above) and Prob. 52 (*V*, 33). *b.* From this result and the molal electrode potentials derived in Prob. 52 (*V*, 33), find the standard free energy of $1Cl^-(aq)$ and of $1Ag^+(aq)$ at 25°.

Prob. 6. — Calculate the free energy of $1Ag_2O(s)$ at 25°. The electromotive force of the cell $H_2(1 \text{ atm.}), KOH(0.1 \text{ wf.}), Ag_2O(s) + Ag(s)$ is 1.172 volt and the free energy of $1H_2O(l)$ is - 56,560 cal. at 25°. *Ans.* - 2510 cal.

Prob. 7. — *a.* Formulate the free energy equation which can be derived from the molal electrode-potential of $I_2(s), I^-(aq)$, and $O_2(g), OH^-(aq)$. *b.* Find the standard molar free energy at 25° of $I^-(aq)$, and of $OH^-(aq)$, referring to the tables of electrode potentials previously given.

Free Energies Derived from Equilibrium Measurements.

Prob. 8. — Calculate the standard free energy of 1NO(g) at 1957°C from the data of *Prob. 63 (VII, 16)*. *Ans.* 13,660 cal.

Prob. 9. — Calculate the free energy of 1HgO(s) at 357°C from its dissociation pressure which is 86 mm. at 357°C .

The Free Energy of a Substance at One Temperature Derived from its Free Energy at Another Temperature.

Prob. 10. — With the aid of the second law free energy equation (*II, 32*), calculate the standard free energy of 1NO(g) at 25° from its free energy at 1957° found in *Prob. 8* and from the heat data of *Prob. 63 (VII, 16)*. *b.* Express its free energy as a function of the temperature. (See *Eq. 66; II, 32*.)

Prob. 11. — Calculate the free energy of 1HgO(s) at 25° from its free energy at 357° found in *Prob. 9* and from the heat data of *Prob. 65 (VII, 16)*, considering the heat of dissociation of solid mercuric oxide into liquid mercury and oxygen to be a linear function of the temperature between 25° and 357° .

Prob. 12. — Describe the separate steps by which the standard free energy of $1\text{CO}_2(\text{g})$ at 25° could be calculated from the equilibrium constant of the reaction $\text{C(s)} + \text{CO}_2(\text{g}) = 2\text{CO(g)}$ measured at 1000°C , that of the reaction $2\text{CO(g)} + \text{O}_2(\text{g}) = 2\text{CO}_2(\text{g})$ measured at 2000°C and from such heat data as are commonly recorded in tables of constants.

Prob. 13. — Calculate the free energy at 25° of 1 at. wt. of monoclinic sulfur from the facts that its conversion into rhombic sulfur at its transition-point (95.5°) is attended by a heat-evolution of 95 cal. and that the atomic heat-capacities of the monoclinic and rhombic forms (*Eastman and McGavock, 1937*) are $3.622 + 0.0068 T$ and $3.522 + 0.0062 T$ cal. per degree, respectively. Tabulate the result with that found in *Prob. 2*.

It remains to be shown how these general methods of determining free energies are applied in developing a systematic set of values of this property for the various substances in their different standard states at a definite temperature, such as 25° . This is illustrated, for the fundamentally important compound water, by the following problem.

Prob. 14. — *The Thermodynamic Constants of Water.* — *a.* Derive from the following experimental data the values of the standard heat-content (as defined in *IX, 1*) of $1\text{H}_2\text{O(s)}$ at 0° , $1\text{H}_2\text{O(l)}$ at 0° , 25° , and 100° ; and derive a temperature-function for

the standard heat content of $1\text{H}_2\text{O}(\text{g})$ from 100° to 2000°C . The formal heat-capacity in cal. per degree of $\text{H}_2\text{O}(\text{l})$ is 18.06 from 0° to 25° ; and 17.95 from 25° to 100° . The fusion of $1\text{H}_2\text{O}(\text{s})$ at 0° absorbs 1438 cal., and the vaporization of $1\text{H}_2\text{O}(\text{l})$ at 100° and 1 atm. absorbs 9730 cal. Values of the molar heat-capacities of $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{H}_2\text{O}(\text{g})$ are recorded in Table II (II, 14). The reaction $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l})$ evolves 68,270 cal. at 25° . b. Derive the standard free energy of $1\text{H}_2\text{O}(\text{g})$ at 1400° , 1800° , and 2200°A from the following values of the percentage dissociation of water-vapor at 1 atm. as determined experimentally by four different investigators.*

Investigator	Abs. Temp.	Percent Dissociated	Investigator	Abs. Temp.	Percent Dissociated
Langmuir	1393	0.0069	Lowenstein	1783	0.182
	1433	0.0103		1863	0.354
	1474	0.0141		1968	0.518
	1550	0.0287	v. Wartenberg	2155	1.18
Nernst, v. Wartenberg	1561	0.0340		2257	1.77

In treating these data, consider, with reference to the principles involved, what temperature function should give nearly a straight-line graph; make a corresponding plot; and draw the best representative graph through the points. c. Calculate from each of the three free energy values found in b, with the aid of the heat-content function found in a, the free energy of $1\text{H}_2\text{O}(\text{g})$ and $1\text{H}_2\text{O}(\text{l})$ at 100°C and 1 atm. From the mean of the values so obtained calculate the free energy of $1\text{H}_2\text{O}(\text{l})$ at 25°C . d. Calculate the free energy of $1\text{H}_2\text{O}(\text{l})$ at 25° from the free energy of $1\text{HgO}(\text{s})$ found in Prob. 11 and the following data: The electromotive force at 25° of the cell $\text{Pt} + \text{H}_2(1 \text{ atm.}), \text{NaOH}(0.01\text{--}0.30 \text{ f.}), \text{HgO}(\text{s}) + \text{Hg}(\text{l})$, has been determined by Brönsted, by Chow, and by Buehrer with concordant results, the mean value being 0.9265 volt. e. Calculate the free energy of $1\text{H}_2\text{O}(\text{l})$ at 1 atm. and 25° from the following data and other data previously given. The equilibrium-constant of the gas reaction $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$ was determined by von Falkenstein to be 0.197 at 723°A , 0.995 at 873°A , and 1.585 at

* These values are based on the assumption that the only reaction of dissociation is $2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$, whereas there is spectroscopic evidence of the existence of molecules of OH in these equilibrium mixtures at concentrations, which, though small, are not negligible in comparison with those of the molecules of O_2 . The correct interpretation of the experimental data would necessitate taking into consideration a second type of dissociation shown by the equation $2\text{H}_2\text{O} = \text{H}_2 + 2\text{OH}$, and the calculations called for in b and c are, for this reason, in error.

923°A. The heat-content of HCl(g) at 25° as found by both Thomsen and by Berthelot is $-22,000$ cal. The free energy of HCl(g) at 1 atm. and at 25° is $-22,790$ cal., as found in Prob. 4. (First find the values of the free-energy decrease attending the gas reaction at 25° corresponding to the three equilibrium-constants, and take their mean.) *f.* Tabulate the three values of the standard free energy of $\text{H}_2\text{O(l)}$ at 25° already found, together with that ($-56,560$ cal.) derived by Lewis and Randall from an exhaustive study of all the data available. *g.* From Lewis and Randall's value of the free energy of water and the value (1.00×10^{-14}) of its ionization-constant at 25°, calculate the standard free energy of $\text{OH}^-(\text{aq})$ at 25°; also the molal potential of the electrode $\text{O}_2(\text{g}), \text{OH}^-(\text{aq})$.

3. Tabulation of Molar Free Energies and Heat-Contents of Some Important Substances. — Tables I and II contain the

TABLE I. STANDARD FREE ENERGIES AND HEAT-CONTENTS OF GASEOUS AND SOLID SUBSTANCES AT 25°.

Gaseous Substances

<i>Substance</i>	<i>Free Energy</i>	<i>Heat-Content</i>	<i>Substance</i>	<i>Free Energy</i>	<i>Heat-Content</i>
H_2	0	0	HI	315	6,150
O_2	32,400	34,000	NH_3	$-3,910$	$-10,980$
H_2O	$-54,507$	$-57,820$	NO	20,850	21,600
H_2S	$-7,840$	$-4,760$	NO_2	11,920	6,845
SO_2	$-69,660$	$-69,000$	N_2O_4	22,640	-90
SO_3	$-85,890$	$-91,600$	HNO_3	$-18,210$	$-34,400$
Cl_2	0	0	CH_4	$-12,800$	$-18,325$
HCl	$-22,692$	$-22,000$	CO	$-32,510$	$-26,140$
Br_2	755	7,590	CO_2	$-94,260$	$-94,237$
HBr	$-12,540$	$-8,305$	C_2N_2	92,000	71,400
I_2	4,630	14,190	HCN	28,910	32,000

Solid Substances

S(rhombic)	0	0	Ag_2O	$-2,395$	$-6,940$
S(monoclinic)	18	82	HgO	$-13,808$	$-21,600$
$\text{Br}_2(\text{liquid})$	0	0	PbO	$-41,000$	$-50,300$
I_2	0	0	AgCl	$-26,187$	$-30,300$
C(graphite)	0	0	HgCl	$-25,137$	$-31,575$
C(diamond)	390	180	TiCl	$-44,164$	$-48,620$
CaH_2	$-34,780$	$-44,500$	PbCl_2	$-74,990$	$-85,710$

TABLE II. STANDARD FREE ENERGIES OF SUBSTANCES IN AQUEOUS SOLUTION AT 25°.

Cation	Free Energy	Substance	Free Energy	Substance	Free Energy
H ⁺	0	H ₂ O(l)	- 56,560	BrO ₃ ⁻	2,300
Li ⁺	- 68,248	HO ⁻	- 37,455	I ₂	3,926
Na ⁺	- 62,588	H ₂ S	- 6,490	I ⁻	- 12,361
K ⁺	- 67,431	HS ⁻	2,980	I ₃ ⁻	- 12,315
Rb ⁺	- 67,473	S ⁻	23,450	HIO	- 23,170
Cu ⁺	10,845	H ₂ SO ₃	- 126,330	IO ₃ ⁻	- 31,580
Cu ⁺⁺	15,912	HSO ₃ ⁻	- 123,920	NH ₄ OH	- 62,860
Ag ⁺	18,448	SO ₃ ⁻	- 116,680	NH ₄ ⁺	- 18,930
Zn ⁺⁺	- 34,984	HSO ₄ ⁻	- 178,935	HNO ₂	- 13,070
Cd ⁺⁺	- 18,348	SO ₄ ⁻	- 176,260	NO ₂ ⁻	- 8,500
Hg ₂ ⁺⁺	36,984	Cl ₂	1,650	NO ₃ ⁻	- 26,500
Tl ⁺	- 7,760	Cl ⁻	- 31,367	H ₂ CO ₃	- 148,810
Tl ⁺⁺⁺	- 48,590	HClO	- 19,018	HCO ₃ ⁻	- 140,000
Sn ⁺⁺	- 6,276	ClO ⁻	- 6,500	CO ₃ ⁻	- 125,760
Pb ⁺⁺	- 5,630	ClO ₂ ⁻	- 250	HCO ₂ H	- 87,920
Fe ⁺⁺	- 20,350	Br ₂	977	HCO ₂ ⁻	- 82,900
Fe ⁺⁺⁺	- 3,120	Br ⁻	- 24,595	HCN	27,520
		HBrO	- 19,680	CN ⁻	39,370

values in calories of the standard free energies and heat-constants of some important substances at 25°. The values are for the most part those derived by Lewis and Randall (in 1923) through a critical analysis of the existing measurements of heat data, equilibrium conditions, and electromotive forces. They relate to that standard state of the substance which is given in the heading, and to that quantity of it which is shown by its formula. The given values appear to have more significant figures than the data warrant; but this is justified by the necessity of making the differences between two or more such values correspond to the free energy or heat-content of reactions derived from them, whose thermodynamic constants are well known.

It is evident from the kind of interrelationship just mentioned that the systemization represents a consistent whole, and that the revision of some one value in the tables based on more recent investigations may necessitate revision of other values. Furthermore, the heat-capacity and other heat-data selected by Lewis and Randall should be employed in calculating the effect

of temperature on the tabulated free energy values. This is clearly shown by the following summarization, in the form of equations, of relations which have already been derived.

$$\Delta C^\circ = \Delta C_0 + \alpha T + \beta T^2 + \dots, \quad (1)$$

$$\Delta H^\circ = \Delta H_0 + \Delta C_0 T + \frac{\alpha}{2} T^2 + \frac{\beta}{3} T^3 + \dots, \quad (2)$$

$$\Delta F^\circ = \Delta H_0 - \Delta C_0 T \ln T - \frac{\alpha}{2} T^2 - \frac{\beta}{6} T^3 - \dots + I T. \quad (3)$$

In these equations ΔC° , ΔH° , and ΔF° represent the increases in heat-capacity (at constant pressure), in heat-content, and in free energy attending the formation of the substance in a specified standard state at T out of the elementary substances in their most stable standard states at the same temperature. The quantities ΔC_0 , α , and β in Eq. 1 are constants obtained from empirical equations expressing the molar heat-capacities of the reacting elementary substances and of the compound substance formed (in the specified standard state) as functions of the temperature. It is evident that this equation is limited in its application to that range of temperature over which the heat-capacity functions of the separate substances are valid. The other equations are subject to the same limitation, since Eq. 2 is derived from Eq. 1 by integration of the first law relation, $d\Delta H^\circ/dT = \Delta C^\circ$, and Eq. 3 from Eq. 2 by integration of the second law free energy equation $d(\Delta F^\circ/T) = -\Delta H^\circ(dT/T^2)$. The quantities ΔH_0 and ΔF_0 are the corresponding constants of integration. The constant ΔH_0 can be calculated by Eq. 2 from a single value of ΔH° which has been determined at any definite temperature. Similarly, the constant I can be evaluated by Eq. 3 from a single known value of ΔF° at a definite temperature.

The free energy functions (Eq. 3) obtained by Lewis and Randall for different substances need not here be given, but the values of ΔH° recorded in Table I as molar heat-contents are in most cases consistent with such functions. The heat-capacity functions adopted for the gaseous substances have already been recorded in Table II (II, 14).

4. Equilibrium Conditions Derived from the Free Energies of the Substances Involved.—When values of the free

energies of substances have been determined by the methods just reviewed, and have been tabulated (as in Tables I and II), these values can be employed, conversely, for calculating transition temperatures, vapor-pressures and solubilities, equilibrium conditions of chemical reactions of all kinds, reduction-potentials, and the electromotive force of voltaic cells. Such calculations are exact, to be sure, only when the gases and solutes involved can be regarded as perfect, unless activity-coefficients at the actual pressures and concentrations are also available. Besides giving a quantitative measure of the constants determining equilibrium conditions, the algebraic sign of the free-energy decrease calculated for any change in state shows the direction in which any system can undergo spontaneous change.

The simplicity with which these various equilibrium conditions can be evaluated with the aid of a system of values of free energies and heat-contents is illustrated by the following problems. These problems are best solved by direct consideration of the general free-energy relations, rather than by the special forms of these relations previously derived for separate cases (such as the Clapeyron and van't Hoff equations).

Prob. 15. — Stability and Transition-Point of Allotropic Forms. — a. Show whether diamond or graphite is the more stable at 25°. *b.* Show whether their transition temperature is above or below 25°. *c.* Determine the transition-point of rhombic and monoclinic sulfur. The atomic-heat-capacities of the two forms between 0° and 100° (as given by *Lewis and Randall*) are $4.12 + 0.0047 T$ and $3.62 + 0.0072 T$, respectively.

Prob. 16. — Vapor-Pressure of Liquids. — a. Find the vapor-pressure of liquid bromine at 25°. *b.* Calculate approximately the vapor-pressure of liquid bromine at 50°; also its boiling-point at 1 atm.

Prob. 17. — Solubility of Gaseous Substances. — a. Calculate the solubility of H_2S gas in water at 25° and 1 atm. *b.* State what other data are needed for calculating approximately its solubility at 50° at 1 atm.; and formulate an expression for making the calculation.

Prob. 18. — Solubility of Non-Ionizing Substances. — Calculate the solubility of iodine in water; *a.* at 25°; *b.* in 0.1 wf. KI solution at 25°, taking into account the formation of I_3^- and assuming the mean ion-activity-coefficients of KI and KI_3 to be equal.

Prob. 19. — Solubility of Substances Completely Ionized in

Solution. — Calculate the solubility in water at 25°; *a.* of silver chloride; *b.* of thallos chloride; and *c.* of lead chloride. Refer to Table III (VII, 6) for mean values of the ion-activity-coefficients required by the ion-attraction theory. *d.* Calculate the partial vapor-pressure of hydrogen chloride in its 4 wf. solution at 25°, taking its mean ion-activity-coefficient to be 1.84 at this concentration. *Ans. d.* 0.018 mm.

Prob. 20. — Criterion of the Stability of Substances. — List the gaseous and solid substances included in the above table which at 1 atm. are unstable with respect to the stable forms of the elementary substances at 1 atm.

Prob. 21. — Dissociation of Gases. — *a.* Calculate the (extremely small) partial pressures of nitric oxide (NO), nitrogen dioxide (NO₂), and nitrogen tetroxide (N₂O₄) which would exist in air at 25° if equilibrium were established between the nitrogen and oxygen and all of these oxides. *b.* Show whether the ratio of NO to N₂, of NO₂ to NO, and of N₂O₄ to NO₂ would increase or decrease with rising temperature.

Prob. 22. — Equilibrium of Gas Reactions. — In a technical method of converting ammonia into nitric acid ammonia mixed with air is passed over red-hot platinum, whereby the reaction $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$ is brought about. *a.* Calculate the equilibrium-constant of this reaction at 800°. As an approximation consider the heat of the reaction to be constant at the value which it has at 25°. *b.* Explain the fact that this equilibrium can be approximately established, even though nitric oxide under these conditions is unstable with respect to nitrogen and oxygen.

Prob. 23. — Equilibrium of Gas Reactions. — *a.* Calculate the equilibrium constant of the Deacon-process reaction $4\text{HCl(g)} + \text{O}_2\text{(g)} = 2\text{Cl}_2\text{(g)} + 2\text{H}_2\text{O(g)}$ at 25°. *b.* Calculate the mol-percents of chlorine and oxygen in the gas which at 1 atm. and 25° would escape from a 4 wf. HCl solution if oxygen at 1 atm. were passed through it in contact with a catalyst so that equilibrium was established. At 25° in 4 wf. HCl the vapor-pressure of the water is 19.6 mm. For other data needed see Prob. 19*d*.

Prob. 24. — Ionization-Constants of Acids. — *a.* Calculate the ionization-constant of the first hydrogen, and that of the second hydrogen of H₂CO₃ at 25°. *b.* Calculate the solubility of carbon dioxide in water at 25° when its partial pressure is 0.0003 atm. (that which prevails in pure air), taking into account the partial ionization of H₂CO₃ into H⁺ and HCO₃⁻ in the resulting solution.

Prob. 25. — Hydrolysis of Salts. — Calculate the hydrolysis of sodium hypochlorite in 0.1 wf. solution, considering that the ion-activity-coefficients are equal to each other.

Prob. 26. — Metathesis of Solid Salts by Solutions of Other Salts. — Calculate the ratio of sodium chloride to sodium hydroxide which results when an excess of solid silver oxide is treated at 25° with dilute sodium chloride solution. Assume the two anions have equal activity-coefficients.

Prob. 27. — Direction of Oxidation Reactions in Solution. — Predict the direction in which each of the following reactions can take place spontaneously at 25° when the concentration of each solute is 1 weight-molal and the pressure of each gas is 1 atm.

- a. $\text{H}_2(\text{g}) + 2\text{Ag}^+ = 2\text{H}^+ + 2\text{Ag}(\text{s})$
- b. $\text{H}_2(\text{g}) + \text{Hg}_2\text{Cl}_2(\text{s}) = 2\text{H}^+\text{Cl}^- + 2\text{Hg}(\text{l})$
- c. $\text{O}_2(\text{g}) + 4\text{Fe}^{++} + 4\text{H}^+ = 4\text{Fe}^{+++} + 2\text{H}_2\text{O}(\text{l})$
- d. $\text{I}_2(\text{s}) + 2\text{Fe}^{++} = 2\text{I}^- + 2\text{Fe}^{+++}$
- e. $\text{Br}_2(\text{aq}) + 2\text{Fe}^{++} = 2\text{Br}^- + 2\text{Fe}^{+++}$
- f. $3\text{H}_2\text{SO}_3(\text{aq}) + \text{ClO}_3^- = 3\text{SO}_4^{--} + \text{Cl}^- + 6\text{H}^+$

Prob. 28. — Equilibrium of Oxidation Reactions in Solution. — When chlorine gas is absorbed by a slight excess of sodium hydroxide all of the chlorine is converted either into NaClO and NaCl or into NaClO₂ and NaCl. a. From the free energy equation show that one of these pairs of products would be formed in very large proportion in case equilibrium were attained. b. Using this conclusion to simplify the calculation, determine the relative proportions of NaClO and NaClO₂ that would be formed at 25° under equilibrium conditions when 1 mol of Cl₂ is absorbed in two liters of 1 wn. NaOH solution, assuming as an approximation that the ions are perfect solutes. c. State what other factor accounts for the fact that the result is different from this when the experiment is actually made. *Ans. b.* $(\text{ClO}_2^-)/(\text{ClO}^-) = 1.6 \times 10^{10}$.

Prob. 29. — Evaluate the reduction-potential at 25° of:

- a. H₂S in water with respect to S(rhombic) and H⁺.
- b. H₂SO₃ in water with respect to SO₄⁻⁻ and H⁺.
- c. H₂O(l) with respect to O₂ gas and H⁺.
- d. State what positions H₂S and H₂SO₃ in acid solution would occupy in Table II (V, 9) as reducing agents; also what position O₂ gas in acid solution would occupy as an oxidizing agent.

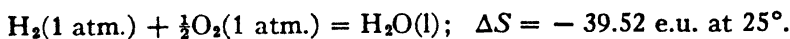
Prob. 30. — Electromotive Force of Voltaic Cells. — Find the electromotive force of the following cells at 25°:

- a. $\text{Fe}(\text{s}), \text{Fe}^{++}(1 \text{ wm.}) \parallel \text{Fe}^{++}(1 \text{ wm.}) \parallel \text{Fe}^{+++}(1 \text{ wm.}) + \text{M.}$
- b. $\text{Hg}(\text{l}) + \text{HgO}(\text{s}), \text{KOH}(0.1 \text{ wf.}), \text{PbO}(\text{s}) + \text{Pb.}$
- c. $\text{O}_2(1 \text{ atm.}), \text{KOH}(0.1 \text{ wf.}), \text{O}_2(1 \text{ atm.}).$

Note: The high value of this last electromotive force shows the large polarization that would result at the oxygen electrode in electrolyzing water if ozone were produced there.

***II. FREE ENERGY OF CHEMICAL CHANGES FROM HEAT AND SPECTROSCOPIC MEASUREMENTS.

5. Molar Entropies and Heat-Contents of Substances Referred to Their Values at the Absolute Zero. — It has already been shown (II, 29) that the entropy-increase ΔS attending any isothermal change in state is related to the corresponding increase in free energy ΔF and in heat-content ΔH as expressed by the equation, $\Delta H - \Delta F = T \Delta S$. As the entropy-increase for a chemical change is evidently the sum of the entropies S_{p} , S_{r} ... of the reaction-products as they exist in the final state diminished by the entropies S_{a} , S_{b} ... of the reacting substances as they exist in the initial state, the entropies of compounds might, like their heat-contents and free energies, be referred to those of the elementary substances taken as zero in their most stable standard state at each temperature. Thus, on this basis, the entropy of $\text{H}_2\text{O}(\text{l})$ at 25° , when computed from its free energy and its heat-content, is found to be -39.52 entropy units (abbreviated e.u. and expressed in calorie/degrees). This fact is conveniently expressed by the entropy equation:



It is, however, becoming customary, because of the thermodynamic relations at the absolute zero discussed in the next article, to express the absolute molar entropy $\tilde{S}^\circ$ and the absolute molar heat-content $\tilde{H}^\circ$ of any substance in each of its different standard states at any temperature T in terms of its molar entropy $\tilde{S}_0$ and molar heat-content $\tilde{H}_0$ as a pure substance in some crystalline state at the absolute zero of temperature. The absolute molar free energy $\tilde{F}^\circ$ of the substance in the standard state at T is then readily evaluated by the relation $\tilde{F}^\circ = \tilde{H}^\circ - T \tilde{S}^\circ$.

Thermochemical and free energy calculations are much simplified by the use of tables of experimentally determined values of $(\tilde{H}^\circ - \tilde{H}_0)$ and $(\tilde{S}^\circ - \tilde{S}_0)$ for different substances in their standard states at a series of temperatures, and of the heats of formation of the substances at a single temperature. Such calculations are based on the aforementioned thermodynamic relations at the absolute zero, and will be considered later.

The first step in the proposed systemization involves the determination of the increase in entropy $(\tilde{S}^\circ - \tilde{S}_0)$ and the increase

in heat-content ($\tilde{H}^\circ - \tilde{H}_0$) when 1 mol of the substance is heated at 1 atm. from the absolute zero to T . The solution of this problem requires a knowledge of the heat-capacity of the substance for the complete range of temperature 0° to T . If the substance undergoes transition, fusion, or vaporization at any intermediate temperature, the discontinuity in the function expressing the heat-capacity must be taken into account, and in addition the increase in entropy and in heat-content attending each isothermal change in state of aggregation must be included.

Precise measurements of heat-capacity have been made in the case of a considerable number of solid substances down to, and even below the boiling-point of hydrogen, 20.4°A ; and these have shown that the molar heat-capacity $\tilde{C}_p$ decreases rapidly at low temperatures, often becoming as small as 0.1 to 1.0 calorie/degree at 20°A . By this fact the evaluation of heat-content is much simplified, since the low-temperature region contributes only a small fraction of the total heat-content at higher temperatures. The evaluation of entropies is similarly simplified, since these heat-capacity measurements have also shown that the ratio $\tilde{C}_p/T$ increases with falling temperature, attains a maximum value, and then decreases rapidly to very small values at extremely low temperatures. Such facts are accounted for by quantum considerations. They are well illustrated by the experimental values of the atomic heat-capacity of solid mercury (*Onnes and Holst, 1914; Simon, 1922-23; Carpenter and Stoodley, 1930*) presented in Table III.

TABLE III. ATOMIC HEAT-CAPACITY OF MERCURY AT LOW TEMPERATURES.

T	$\tilde{C}_p$	$1000 \tilde{C}_p/T$	T	$\tilde{C}_p$	$1000 \tilde{C}_p/T$
3.45	0.105	30.4	52.9	5.116	96.7
5.37	0.27	50.3	67.9	5.597	82.4
10.17	1.15	113.1	87.5	5.800	66.3
12.35	1.44	116.5	109.4	5.984	54.7
13.35	1.57	117.6	130.8	6.165	44.7
20.3	2.526	124.4	191.7	6.503	33.9
27.5	3.459	125.8	210.	6.54	31.1
30.3	3.743	123.6	225.	6.68	29.7
37.7	4.347	115.3	234.	6.77	28.9

The general procedure for evaluating the absolute entropies and heat-contents on the basis of the preceding considerations is indicated in Prob. 31. For the detailed methods that have been used to estimate, if necessary, the entropy and heat-content values at temperatures below which heat-capacity measurements are not available, reference must be made to more complete treatises.

Prob. 31. — Evaluation of Absolute Entropies and Heat-Contents of Substances from Heat Data. — The atomic heat of fusion of mercury is 557 cal. at its melting-point 234°A ; its atomic heat of vaporization is 14,160 cal. at the boiling-point 630°A ; and its atomic heat-capacity at constant pressure as a liquid may be taken as $7.2 - 0.002 T$ (*Carpenter and Stoodley, 1930*) between 234 and 298°A , and constant at 6.6 calorie/degrees between 298° and 630°A . With the aid of these heat data, and the atomic heat-capacities of solid mercury recorded in Table III, proceed as directed to find the absolute molar entropy and heat-content of mercury in the series of standard states indicated below. *a.* Calculate the entropy-increase and the heat-content increase for each of the following changes in state:

(1) $\text{Hg(l)}\ 298^{\circ}\text{A},\ 1\ \text{atm.} = \text{Hg(g)}\ 630^{\circ}\text{A},\ 1\ \text{atm.}$

(2) $\text{Hg(s)}\ 234^{\circ}\text{A},\ 1\ \text{atm.} = \text{Hg(l)}\ 298^{\circ}\text{A},\ 1\ \text{atm.}$

b. Evaluate the increase in entropy ($\tilde{S}^{\circ} - \tilde{S}_0$) attending the change in state $\text{Hg(s)}\ 0^{\circ}\text{A},\ 1\ \text{atm.} = \text{Hg(s)}\ 234^{\circ},\ 1\ \text{atm.}$, by one of the following graphical methods of evaluating the integral $\int_0^{234} C_p dT/T$. Either plot the corresponding values of $\tilde{C}_p/T$ as ordinates against those of T as abscissas, or plot values of $\tilde{C}_p$ against those of $\log T$, and in each case determine the area below a smooth (best representative) curve drawn between the experimental points. *c.* Find the increase in heat-content ($\tilde{H}^{\circ} - \tilde{H}_0$) attending this same change in state by a graphical method of evaluating the integral $\int_0^{234} C_p dT$. *d.* Finally, evaluate and tabulate the absolute atomic entropy $\tilde{S}^{\circ}$, and heat-content $\tilde{H}^{\circ}$ of mercury (in terms of $\tilde{S}_0$ and $\tilde{H}_0$) in each of the following standard states: Hg(s) at 234°A ; Hg(l) at 234°A ; Hg(l) at 298°A ; Hg(l) at 630°A ; and Hg(g) at 630°A .

Prob. 32. — General Expressions for the Absolute Entropy of Perfect Gases. — *a.* Formulate a differential equation for the increase $d\tilde{S}$ in the molar entropy of a perfect gas by a temperature-increase dT and a pressure increase dp , and the corresponding indefinite integral. *b.* Formulate a second general expression for the

absolute molar entropy $\tilde{S}$ of a substance existing as a perfect gas at temperature T and pressure p , considering that at 1 atm. it melts at T_f and boils at T_b , that it has molar heat-capacities $\tilde{C}_s$, $\tilde{C}_l$, and $\tilde{C}_g$, variable with the temperature, in the solid, liquid, and gaseous states, that its molar heats of fusion and vaporization are $\Delta\tilde{H}_f$ and $\Delta\tilde{H}_v$, and that its molar entropy as a solid at 1 atm. and 0°A is $\tilde{S}_0$.

6. Thermodynamic Relations at the Absolute Zero. The Third Law of Thermodynamics. — Measurements of the heat-capacities of crystalline substances at low temperatures show that these decrease rapidly with the temperature and attain such small values as to make it probable that they become negligible at the absolute zero. Since the quantum theory also leads to this conclusion, it may be regarded as a fundamental principle that *the heat-capacities of pure crystalline substances become zero at the absolute zero*. Therefore also for any isothermal change in state involving such substances at the absolute zero:

$$\Delta C_p = 0; \quad \text{and} \quad \frac{d(\Delta H)}{dT} = 0 \left(\text{since } \Delta C_p = \frac{d(\Delta H)}{dT} \right).$$

The second-law free energy equation,

$$\frac{d(-\Delta F)}{dT} = \frac{\Delta H - \Delta F}{T},$$

shows that, as T approaches zero, ΔH must approach ΔF , unless the improbable assumption be made that $d(-\Delta F)/dT$ becomes infinite. Or expressed in words, *the heat-content change is equal to the free energy change for any change in state at the absolute zero*.

It does not follow from this equation that the free energy coefficient, $d(-\Delta F)/dT$, approaches zero at the absolute zero; for the second member of the equation then assumes the indeterminate form $0/0$. Nevertheless, the principle that, for reactions between pure crystalline substances, $d(\Delta H)/dT = 0$ at $T = 0$, taken in connection with the principle that $\Delta H = \Delta F$ at $T = 0$, suggests that the corresponding free energy coefficient may also approach zero at the absolute zero; that is, that $d(-\Delta F)/dT = 0$ at $T = 0$.

Since the entropy-increase ΔS for an isothermal change in state is expressed by the equation $\Delta S = (\Delta H - \Delta F)/T$, this is

equivalent to the statement that *the entropy change is zero for any change in state at the absolute zero involving only pure crystalline substances*. That is,

$$\Delta S = 0. \quad (4)$$

This principle is sometimes called from its discoverer (1906) the *Nernst heat-theorem*. It states that at the absolute zero the molar entropy $\tilde{S}_0$ of any pure compound substance $A_e E_e$ in the crystalline state is equal to the sum, $a \tilde{S}'_0 + e \tilde{S}''_0$, of the atomic entropies of its constituent elements (in the crystalline state). The constants $\tilde{S}_0$, $\tilde{S}'_0$, and $\tilde{S}''_0$ are thermodynamically indeterminate, but for convenience in thermodynamic calculations, $\tilde{S}'_0$ and $\tilde{S}''_0$ and hence also $\tilde{S}_0$ may be arbitrarily considered to be zero.

An explanation of the Nernst heat-theorem was sought by considering the entropy-concept from the standpoint of statistical mechanics, and the conclusion was drawn (*Planck, 1911*) that the above arbitrary assumption of zero entropy at the absolute zero is in general true. Accordingly this principle is often expressed mathematically as follows:

$$\tilde{S}_0 = 0; \quad \text{and hence} \quad \tilde{F}_0 = \tilde{H}_0 = \tilde{E}_0 = \tilde{A}_0 \text{ (at } T=0\text{)}. \quad (5)$$

Here $\tilde{F}_0$, $\tilde{H}_0$, $\tilde{E}_0$, and $\tilde{A}_0$ represent absolute values of the molar free energy, heat-content, energy-content, and work-content of any pure substance in the crystalline state at the absolute zero.

The Nernst heat-theorem thus stated is commonly called the *third law of thermodynamics*. Values of the molar entropies of substances based on Eq. 5, and computed from heat-data (as in Prob. 31), will be called *absolute entropies*.

7. The Free Energy Decrease Attending Chemical Changes at Any Temperature Calculated with Aid of the Third Law of Thermodynamics. — The great significance of the third law is that it makes possible the evaluation from heat data alone of the free energy changes attending changes in state at any temperature, and hence of the equilibrium-constants of chemical reactions. The following statements show how the calculations are made for any definite reaction at a definite temperature T .

Since the third law requires that at the absolute zero the entropies of all crystalline compounds be zero, like those of the

elementary substances, the absolute molar entropies of the compounds involved in the reaction, whether they are solid or gaseous, can be found, with the aid of their heat-capacities between 0 and T° and their heats of fusion, vaporization, and transition, in the way described in Prob. 31. The entropy-increase attending any definite chemical change at the temperature T would then be found by subtracting the sum of the entropies of the reaction-products from the sum of those of the reacting substances; thus for the change in state, $aA + bB \cdots = eE + fF \cdots$, each substance being in one of its standard states, the entropy-increase ΔS° would be given by the following equation in which $\tilde{S}_a^\circ, \tilde{S}_b^\circ \cdots$ are the molar entropies at T of the substances in their respective standard states:

$$\Delta S^\circ = e \tilde{S}_e^\circ + f \tilde{S}_f^\circ \cdots - a \tilde{S}_a^\circ - b \tilde{S}_b^\circ \cdots$$

From the value of ΔS° thus found and the calorimetric value of the standard heat-content increase ΔH° , the corresponding free energy increase ΔF° can be calculated by the thermodynamic relation, $\Delta F^\circ = \Delta H^\circ - T \Delta S^\circ$. Finally the equilibrium-constant K of the chemical reaction can be calculated by the familiar equation, $-\Delta F^\circ = R T \ln K$.

Prob. 33. — Free Energy and Equilibrium of Chemical Reactions. — a. Determine the entropy of 1HgO(s) at 298°A from the following values of its formular heat-capacity $\tilde{C}_p$ at constant pressure (*Günther, 1916; Russell, 1912*) by plotting $\tilde{C}_p/T$ against T , as in Prob. 31. (Note that these data relate to red mercuric oxide, and that the accepted value (*I. C. T.*, 5, 90, 1929) of the entropy of 1HgO at 298°A is 16.6 e.u.)

T	$\tilde{C}_p$	$1000 \tilde{C}_p/T$	T	$\tilde{C}_p$	$1000 \tilde{C}_p/T$
25.1	1.973	78.6	74.7	5.775	77.3
28.1	2.378	82.9	137.5	7.66	55.9
35.7	3.093	86.6	236.0	9.70	41.1
40.5	3.615	89.3	296.2	10.85	36.7

b. Find also the entropy of 1HgO(s) at 630°A , taking its formular heat-capacity equal to $9.0 + 0.006 T$ above 298°A . *c.* From the entropy of 1HgO(s) at 298°A obtained in *a*, that of 1Hg(l) at 298°A found in Prob. 31, and that (49.1 e.u.) of $1\text{O}_2\text{(g)}$ derived in

a similar way, and from the fact that the formation of 1HgO(s) at 298°A evolves 21,600 cal., calculate the standard free energy of formation ΔF° of 1HgO(s) at 298°A . *d.* From the facts that at 298°A the electromotive force of the cell, $\text{H}_2(1 \text{ atm.}), \text{KOH}(0.1 \text{ wf.}), \text{HgO(s)} + \text{Hg(l)}$ is 0.9265 volt, and the standard free energy of formation of $\text{1H}_2\text{O(l)}$ is $-56,720 \text{ cal.}$, calculate the standard free energy of formation of 1HgO(s) at 298°A ; and find the difference between this value and that obtained in *c.* *e.* From the entropy of 1HgO(s) at 630°A found in *b*, that of 1Hg(g) at 1 atm. and 630°A found in Prob. 31, and that of $\text{1O}_2(\text{g})$ at 1 atm. and 630°A , which is 54.6 e.u., find the entropy-increase at 630°A for the change in state $\text{HgO(s)} = \text{Hg(g)} + \frac{1}{2}\text{O}_2(\text{g})$, each at 1 atm. *f.* From this entropy-increase and the heat-content increase (35,260 cal.) for this change in state, calculate the dissociation-pressure of HgO at 630°A in mm. (which has been found by direct measurement to be 86 mm.).

The validity of the methods of calculating free energies on the basis of the third law of thermodynamics is verified by precise heat-capacity measurements at low temperatures. A few of the more reliable results are given in Table IV in which values in calories of $T \Delta S$ at 25° computed by the third law are compared with values of $\Delta H - \Delta F$ derived from measurements of heats of reaction and of equilibria or electromotive forces.

TABLE IV. DATA TESTING THE THIRD LAW OF THERMODYNAMICS.

<i>Change in State at 298°A</i>	$\Delta H^\circ - \Delta F^\circ$	$T \Delta S^\circ$	<i>Difference</i>
$\text{S(rhombic)} = \text{S(monoclinic)}$	77	47	30
$\text{Sn(gray)} = \text{Sn(white)}$	557	477	80
$\text{Ag(s)} + \frac{1}{2}\text{Hg}_2\text{Cl}_2(\text{s}) = \text{AgCl(s)} + \text{Hg(l)}$	2325	2474	- 149
$\frac{1}{2}\text{Pb(s)} + \text{AgCl(s)} = \frac{1}{2}\text{PbCl}_2(\text{s}) + \text{Ag(s)}$	- 1282	- 1058	- 224
$\frac{1}{2}\text{Pb(s)} + \text{AgI(s)} = \frac{1}{2}\text{PbI}_2(\text{s}) + \text{Ag(s)}$	- 1192	- 1192	0
$\text{Ag(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) = \text{AgCl(s)}$	- 4084	- 4054	- 30

8. The Entropy of Perfect Monatomic Gases. — The effect of temperature and pressure on the molar entropy of any perfect gas was found in Prob. 32 to be expressed by the equation :

$$d\tilde{S} = \tilde{C}_p d \ln T - R d \ln p.$$

In the case of a monatomic gas, $\tilde{C}_p$ is constant and equal to $2.5 R$. For this case the integral of this equation becomes,

$$\tilde{S} = \tilde{S}_0 + 2.5 R \ln T - R \ln p.$$

Quantum theory considerations (*Sackur, 1911; Telrode, 1912; ...*), which can not be presented here, have led to the important conclusion that the integration constant $\tilde{S}_0$ in this equation is determined solely by the molecular weight of the gas; and that its value is such that the absolute *molar entropy in calorie/degrees of a perfect monatomic gas of molecular weight M at the temperature T and the pressure p* (expressed in atmospheres) is given by the equation:

$$\tilde{S}^\circ = -2.30 + 1.5 R \ln M + 2.5 R \ln T - R \ln p. \quad (6)$$

The validity of this equation has been tested by comparing (as illustrated by Prob. 34) the entropy values to which it leads with those obtained by calculating the entropy increase, up from the absolute zero, by means of data on the heat-capacity and heats of fusion and vaporization, for various elementary substances forming monatomic vapors. Table V shows the results of such a comparison in the case of some of the substances for which reliable heat data exist. The entropies are given in calorie/degrees, and refer to the substance in the state of a perfect gas at 1 atm.; the values being calculated to correspond to this condition when the substance actually exists as a solid or liquid at 1 atm. and at the given temperature. It will be noted that the term $2.5 R \ln T$ is simply the change in entropy produced by changing the temperature of the gas corresponding to the integral of $\tilde{C}_p d \ln T$, since for a monatomic gas $\tilde{C}_p = 2.5 R$; also that the term $-R \ln p$ is the usual expression for changing the pressure of any perfect gas from 1 to p atmospheres.

TABLE V. MOLAR ENTROPIES OF PERFECT MONATOMIC GASES IN STANDARD STATE AT 25°.

Substance	Calorimetric	Entropy-Equation	Difference
Mercury	42.1	41.80	0.3
Cadmium	39.3	40.07	- 0.8
Zinc	38.46	38.46	0
Argon	36.8	36.99	- 0.2
Neon	35.0	34.96	0

The above entropy equation also furnishes (as shown in Prob. 35) another method of evaluating the entropies of liquid

and solid elementary substances which form monatomic vapors, as do most of the metals. This method has the advantage that it does not involve the use of low-temperature heat data, accurate values of which are difficult to obtain. The equation should be used advisedly, however, since the vapors of the alkali metals, the monatomic halogens, and the monatomic form of certain other elements show appreciable deviations from it. Such deviations are explicable in terms of quantum mechanics, and may be calculated if the nature of the lower electronic quantum states of the atom is known.

Prob. 34. — Test of the Entropy Equation for Monatomic Gases. — *a.* Calculate by the equation given in the text the entropy of 1Hg(g) at 1 atm. and 357°C ; and find its divergence from the value computed in Prob. 31 from heat data. *b.* Calculate by the equation and also from the entropy value at 357°C found in Prob. 31 values of the entropy of 1Hg(g) at 1 atm. and 25°C . Compare these values with those given in the table.

Prob. 35. — Derivation of the Entropies of Liquid and Solid Elementary Substances Forming Monatomic Vapors. — *a.* Calculate the atomic entropy of liquid zinc at its boiling-point (907°C) at which its atomic heat of vaporization is 27,430 cal. *b.* Calculate the atomic entropy of solid zinc at 25° . At its melting-point 419.5°C its atomic heat of fusion is 1595 cal. The atomic heat-capacity of solid zinc between the melting-point and 25° is $5.25 + 0.0027 T$, and that of liquid zinc between the melting-point and boiling-point is $7.59 + 0.00055 T$ cal./deg. (The value computed from low temperature heat-capacities is 9.95 eu.)

9. The Entropy and Heat-Content of Gases from Spectroscopic Data. — It has already been shown that the theorem of equipartition of energy (III, 25) supplies only a partial explanation of the heat-capacities of polyatomic gases, and that the limitations of this theorem with respect to the rotational and vibrational energies of the molecules can be accounted for by the theory of quantum mechanics. The quantization of the rotational energy of rigid diatomic molecules was briefly treated in III, 26. It is not within the scope of this book to extend this treatment to include the vibrational energies of diatomic molecules or to more complex molecules. By so doing, it is possible to compute from spectroscopic data the summation of the rotational, vibrational, and electronic energies of all the molecules in

one mol of a definite gaseous molecular species at different temperatures. By addition of the translational kinetic energies, equal to $\frac{3}{2} R T$, to this summation is obtained the difference ($\tilde{E}^\circ - \tilde{E}_0$) between the molar energy of this species in the state of a perfect gas at the temperature T and at the absolute zero. Its heat-capacity (in the state of a perfect gas) and related thermodynamic properties can then be derived from the change of the total energy with the temperature. For example, the difference ($\tilde{S}^\circ - \tilde{S}_0$) between the molar entropy of a gaseous substance in its standard state at T and at the absolute zero can be evaluated from spectroscopic data alone. In this case, as in that of a perfect monatomic gas, the integration constant $\tilde{S}_0$ is calculable from the molecular weight of the gas. The theoretical considerations involved can not be here presented, but it may be pointed out that values of entropy thus obtained should agree with those calculated from calorimetrically determined heat-capacities, heats of fusion and vaporization by the methods described in Prob. 31.

In Table VI are presented values of the molar entropy $\tilde{S}^\circ$, the molar heat-content $\tilde{H}^\circ - \tilde{H}_0$ (referred to its value in the standard hypothetical gas state at 0°A) and the heat of formation $\Delta\tilde{H}^\circ$ (or molar heat-content as defined in IX, 1) for a limited number of molecular species in the state of a perfect gas at 25°C and 1 atm. The entropy values were obtained from the more recent precise calorimetric determinations and interpretation of spectroscopic data. In most cases the calorimetric and spectroscopic values agree within the limits of experimental error. In the other cases (indicated by an asterisk) the spectroscopic values should be given preference. The observed discrepancies can be accounted for by theoretical considerations.

The molar entropies and heats of formation recorded in the third and fifth columns of the table afford a basis for calculating the standard free energy ΔF° at 25° of any reaction involving these gases. Furthermore, from the absolute and relative values of the molar heat-content recorded in the fourth and fifth columns may be calculated the thermodynamic constant ΔH_0 , which represents the standard heat of the gas reaction at 0°A . Since, at the absolute zero, the heat-content change is equal to the free energy change for any change in state (IX, 6), this constant also represents the standard free energy ΔF_0 of the

TABLE VI. MOLAR ENTROPY AND HEAT-CONTENT OF GASES IN STANDARD STATE AT 25°.

Gas	$\tilde{S}^\circ$ (Calorimetric)	$\tilde{S}^\circ$ (Spectroscopic)	$\tilde{H}^\circ - \tilde{H}_0$ (Spectroscopic)	$\Delta\tilde{H}^\circ$ (Calorimetric)
H ₂	29.7*	31.23	2027	0
O ₂	49.1	49.03	2072	0
N ₂	45.9	45.79	2075	0
Cl ₂	52.8	53.3	2190	0
Br ₂	59.8	58.7	2324	7,650
I ₂	62.3	62.3	2415	14,910
HCl	44.5	44.66	2066	- 22,060
HBr	47.6	47.48	2066	- 8,650
HI	49.5	49.40	2066	5,910
H ₂ O	44.3*	45.10	2371	- 57,800
H ₂ S	49.0	49.15	2379	- 5,300
CO	46.2*	47.32	2075	- 27,060
CO ₂	51.1	51.08	2238	- 94,670
CH ₄	44.5	44.5	2391	- 18,460
NO	49.7*	50.34	2190	21,600
N ₂ O	51.4*	52.58	2291	19,650
NH ₃	45.9	46.03	2397	- 11,000
SO ₂	59.2	59.40	2519	- 70,920

The entropy arising from nuclear spin, and the entropy of mixing of isotopes are not included in these values. The heats of formation $\Delta\tilde{H}^\circ$ are those compiled by Bichowsky and Rossini (1936). For the carbon compounds a correction was made (see foot-note II, 27) for the heat of transition of diamond to graphite, but $\Delta\tilde{H}^\circ$ was considered in all cases to have the same value at 25° as at 18°.

reaction at 0°A. Such calculations are illustrated by the following problems.

Free Energy Values from Spectroscopic and Heat Data.

Prob. 36. — *a.* Calculate the standard free energy ΔF° of the reaction $2\text{CO(g)} + \text{O}_2\text{(g)} = 2\text{CO}_2\text{(g)}$ at 25°C. *b.* Calculate the thermodynamic constant ΔH_0 , which represents the standard heat (equal to the standard free energy ΔF_0) of the same reaction at 0°A.

Prob. 37. — *a.* From the data of Table VI and the vapor-pressure of water, calculate the electromotive force at 25° of the cell, H₂(1 atm.), KOH(0.1 wf.), O₂(1 atm.). *b.* From this value and the ionization-constant of water, calculate the molal reduction potential at 25° of the reaction $4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4\text{E}^-$.

The calculation of the molar entropy and heat-content of a gas of definite molecular complexity in its standard state from spectroscopic data is not limited to any specified temperature. For example, in Table VII are recorded spectroscopically determined values of the molar entropies of the gaseous species, H_2 , O_2 , Cl_2 , N_2 , NH_3 , H_2O , and HCl in the state of a perfect gas at 1 atm. and at a series of temperatures. In tables of this kind, it has been found convenient to record values of $(\tilde{F}^\circ - \tilde{H}_0)/T$

TABLE VII. MOLAR ENTROPIES AND FREE ENERGIES OF GASES IN THE STANDARD STATE AT A SERIES OF TEMPERATURES.

T	500°	600°	700°	800°	1000°	1200°	1500°	
$\tilde{S}^\circ$	34.826	36.101	37.184	38.115	39.721	41.053	42.739	H_2
$-\frac{\tilde{F}^\circ - \tilde{H}_0}{T}$	27.965	29.218	30.280	31.204	32.752	34.027	35.605	
$\tilde{S}^\circ$	52.740	54.117	55.314	56.381	58.214	59.753	61.674	O_2
$-\frac{\tilde{F}^\circ - \tilde{H}_0}{T}$	42.691	46.984	48.089	49.062	50.715	52.095	53.826	
$\tilde{S}^\circ$	57.656	59.271	60.603	61.765	63.725	65.346	67.362	Cl_2
$-\frac{\tilde{F}^\circ - \tilde{H}_0}{T}$	49.865	51.298	52.531	53.614	55.453	56.979	58.876	
$\tilde{S}^\circ$	49.401	50.701	51.822	52.815	54.527	55.978	57.807	N_2
$-\frac{\tilde{F}^\circ - \tilde{H}_0}{T}$	42.431	43.705	44.786	45.729	47.322	48.646	50.301	
$\tilde{S}^\circ$	50.761	52.602	54.346	55.915	58.757	61.296	64.673	NH_3
$-\frac{\tilde{F}^\circ - \tilde{H}_0}{T}$	42.249	43.826	45.209	46.450	48.634	50.535	53.033	
$\tilde{S}^\circ$	49.315	50.864	52.216	53.425	55.542	57.380	59.783	H_2O
$-\frac{\tilde{F}^\circ - \tilde{H}_0}{T}$	41.296	42.765	44.020	45.121	46.999	48.579	50.586	
$\tilde{S}^\circ$	48.25	49.60	50.72	51.70	53.36	54.75	56.50	HCl
$-\frac{\tilde{F}^\circ - \tilde{H}_0}{T}$	41.321	42.588	43.663	44.597	46.171	47.472	49.096	

The values relate to the equilibrium mixture of isotopes and do not include the effect of nuclear spin.

(which is evidently equal to $(\tilde{F}^\circ - \tilde{F}_0)/T$) in place of values of $(\tilde{H}^\circ - \tilde{H}_0)$, as in Table VI. Such tabulation for different gases covering a wide range of temperature greatly facilitates the calculation of the free energies, equilibrium constants, and heats of gaseous reactions at different temperatures. Calculations of this kind are illustrated by the following problems.

Prob. 38. — Interrelationship of Thermodynamic Properties. — Derive an expression for $(\tilde{F}^\circ - \tilde{H}_0)/T$ in terms of T , $\tilde{S}^\circ$, and $(\tilde{H}^\circ - \tilde{H}_0)$ for any definite molecular species.

Equilibrium of Gas Reactions from Spectroscopic and Heat Data.

Prob. 39. — a. By reference to Table VI, calculate the standard heat ΔH_0 (or standard free energy ΔF_0) of the reaction $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) = 1\text{NH}_3(\text{g})$ at 0°A . *b.* From this value and the data of Table VII, calculate the standard free energy ΔF° of the reaction at 600° and 700°A . *c.* Calculate the corresponding values of the equilibrium-constant, and compare them with those, 0.0382 at 600° , and 0.0090 at 700°A , obtained from direct measurements (*Larson and Dodge, 1923-24*) of the equilibrium conditions of the reaction at different temperatures and pressures.

Prob. 40. — a. Calculate the standard free energy ΔF° of the reaction $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = 2\text{HCl}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$, and the corresponding value of its equilibrium-constant at 600° and at 700°A from the data of Tables VI and VII, and compare the values thus found with those given in Prob. 14 (IX, 2).

Heats of Reaction at Different Temperatures from Heats of Formation at 25° and Spectroscopic Data.

Prob. 41. — By reference to Table VII and the results of Prob. 40, calculate the standard heat ΔH° of the reaction $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = 2\text{HCl}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ at 600° and 700°A .



NOTATION

a	activity; area.	n	number of molecules.
a, b	van der Waals constants.	$\bar{n}$	number of molecules in one ccm.
c	molal concentration; molality.	$\tilde{n}$	number of molecules in one mol.
d	density.	p	pressure.
d	differential.	r	radius.
d	diameter.	s	solubility.
e	electron charge.	t	time.
e	base of natural logarithms.	t	centigrade temperature.
f	force.	u	velocity.
f	fugacity.	v	volume.
g	gravity-acceleration.	$\bar{v}$	specific volume.
h	height; hydrolysis.	$\tilde{v}$	molar volume.
h	Planck's constant.	x, y, z	coördinates.
i	molar-coefficient.	z	impact frequency in molecules per sq. cm.
j	rotational quantum number.	$\bar{z}$	collision frequency of molecules in one ccm.
k	Boltzmann's constant.	z	collision frequency of a single molecule.
k	specific reaction-rate.	z	electrovalence of ions.
l	distance; length.		
$\bar{l}$	mean free path.		
m	mass.		
n	number.		
A	atomic weight; work-content.	H	heat-content.
A, B	constants.	$\tilde{H}$	molar heat-content.
B°	molal boiling-point raising.	I	moment of inertia.
B_0	mol-ratio boiling-point raising.	K	equilibrium-constant.
C	heat-capacity.	K	kinetic energy.
$\bar{C}$	specific heat-capacity.	M	molecular weight.
$\tilde{C}$	molar heat-capacity.	N	number of mols.
E	energy; energy-content.	P	osmotic pressure.
F	free energy.	Q	heat absorbed.
$\tilde{F}$	molar free energy.	R	gas-constant.
G	extensive property.	S	entropy.
$\tilde{G}$	molar property.	$\tilde{S}$	molar entropy.
G°	molal freezing-point lowering.	T	absolute temperature.
G_0	mol-ratio freezing-point lowering.	W	work.
		X	mol-fraction.
		Z	impact frequency in mols per sq. cm.

C	normal concentration; normality.	L	conductance.
$\bar{C}$	normality in ml.	$\bar{L}$	specific conductance.
E	electromotive force.	N	number of equivalents or faradays.
E	electrode-potential.	Q	quantity of electricity.
E°	molal electrode-potential.	R	resistance.
F	faraday.	T	transference number.
I	current-strength.	U	ion-mobility.
K	dielectric constant.	V	potential.
α	activity-coefficient.	Λ	equivalent conductance.
α, β	coefficients.	μ	ionic strength.
γ	dissociation or ionization.	ν	frequency.
Δ	increment.	π	circumference-diameter ratio.
η	viscosity.	Σ	summation.
λ	wave-length.		

INDEX OF AUTHORS

AMAGAT, 187.
 Andrews, 237.
 Arrhenius, 298, 426.
 Avogadro, 36, 128.

BATSON, 232.
 Baxter, 22.
 Baynes, 164.
 Beattie, 187, 193, 284.
 Beckmann, 220, 226, 232, 233.
 Benton, 489.
 Berkley, 239.
 Berthelot, 517.
 Berthelot, D., 190.
 Bichowsky, 68.
 Birge, 146.
 Bodenstein, 408, 424.
 Boltzmann, 128, 142, 167, 177.
 Boynton, 164.
 Boyle, 13, 36.
 Bray, 399.
 Bridgeman, 187, 193, 284, 486.
 Brönsted, 516.
 Bryan, 142.
 Buckingham, 151.
 Buehrer, 516.
 Bunsen, 151.
 Burks, 187.

CANNIZZARO, 135.
 Carnot, 105, 108.
 Carpenter, 524, 525.
 Carver, 233.
 Charles, 36.
 Chow, 516.
 Clapeyron, 117, 207.
 Clausius, 114, 141, 151.
 Collins, 198, 199.
 Cottle, 404.
 Coulomb, 301.

DALTON, 14, 137.
 Daniels, 426.
 Debye, 300, 303, 307, 348.
 Dodge, 535.
 Drake, 489.
 Duhem, 251, 276.
 Dumas, 129.
 Dunphy, 225.

EASTMAN, 515.
 Edwards, 151.
 Ehlers, 371.
 Einstein, 11.
 Eucken, 150, 173.

FALES, 411.
 Falk, 327, 347.
 von Falkenstein, 516.
 Faraday, 89, 321.
 Flügel, 232.
 Frandsen, 198, 199.
 Frazer, 219, 239, 240.

GARNER, 373.
 Gay-Lussac, 36, 61, 127.
 Gibbs, 95, 276, 291, 393, 476.
 Graham, 150.
 Green, 422.
 Günther, 528.

HARNED, 371.
 Hartley, 239.
 Helmholtz, 44, 95, 115, 393.
 Henry, 247.
 Herzfeld, 154, 159, 424.
 Heuse, 199.
 Hildebrand, 214, 215, 267.
 Hinshelwood, 422, 431.
 Hittorf, 326, 328.
 Hofmann, 130.
 Holland, 239, 240.
 Holst, 524.
 Hönigschmid, 22.
 Hüchel, 300, 303, 307, 348.
 Humphreys, 169.

INNES, 226.
 Izard, 386.

JOHNSTON, 237, 426.
 Joule, 44, 61, 196, 197.

KEESOM, 194, 199.
 Kékulé, 135.
 Kelvin, 113.
 Keyes, 187, 190, 194, 198, 199.
 Knudsen, 150.
 Kohlrausch, 342.
 Kohman, 237.

- Kolthoff, 457.
Kraus, 232.
Kundt, 172.
Kunz, 374.
- LANDOLT, 10.
Langmuir, 516.
Laplace, 172.
Larsen, 535.
Lavoisier, 10.
Lewis, G. N., 75, 96, 202, 275, 283,
285, 304, 517, 518, 519, 520.
Liesche, 220.
Lind, 424.
Livingston, 399.
Longworth, 328, 331, 334, 343.
Lovelace, 219.
Löwenstein, 516.
Lummer, 173.
- MACH, 110.
MacInnes, 328, 331, 439.
Manley, 11.
Maxwell, 142, 151, 162, 177, 432.
Mayer, 44.
McGavock, 515.
Menten, 415.
Meyer, 406.
Meyer, O. E., 164.
Meyer, Victor, 130.
Michaelis, 415.
Millikan, 19, 146.
Milner, 300.
Morley, 21.
Morrell, 44.
Morse, 239, 240.
Moseley, 18.
- NELSON, 415.
Nernst, 516, 527.
Newton, 9, 45.
Noyes, 299, 327, 347, 348, 373, 404,
417.
- OHM, 338.
Onnes, 524.
Onsager, 341.
Ostenberg, 199.
Ostwald, 1, 2, 104.
- PFEFFER, 239.
Planck, 105, 179, 527.
Poisson, 308.
Pringsheim, 173.
Proust, 13.
- RAMSEY, 220.
Randall, 75, 202, 275, 297, 304, 517,
518, 519, 520.
Raoult, 204, 216, 231.
Richards, 22, 233.
Roebuck, 199.
Rogers, 219.
Rosanoff, 225.
Rosenblum, 457.
Rossini, 68, 198, 199.
Russell, 528.
Rutherford, 18.
- SACKUR, 530.
Sakurai, 227.
Saxton, 233.
Scatchard, 314.
Scheel, 199.
Schmidt, 264.
Schubert, 415.
Schumb, 233.
Scott, 297.
Shedlovsky, 439.
Sherrill, 386.
Simon, 524.
Smallwood, 154, 159.
Sørensen, 381.
Stas, 22.
Stokes, 20.
Stoodley, 524, 525.
- TAYLOR, 154, 159.
Tetrode, 530.
Thomsen, 517.
Thomson, 196, 197.
Tolman, 154, 165.
Trouton, 214.
- VAN DER WAALS, 185.
van Santen, 194, 199.
van't Hoff, 204, 231, 239, 250, 252,
297, 427, 471.
- WALDEN, 348.
Warburg, 172.
von Wartenberg, 516.
Washburn, 12, 198, 199, 337.
Wason, 417.
Worthington, 238.
- YOST, 418.
- ZAWIDZKI, 256, 261, 277.

INDEX OF SUBJECTS

In this index formal statements of laws or principles and their formulations in equations are itemized under the heading "laws, principles, fundamental equations." Definitions of "concepts, properties, and fundamental constants," values of the "constants of chemical substances," and definitions and values of "units" are entered under these headings, respectively.

- ACIDS and Bases,
 - dibasic acids, ionization, 449-451.
 - displacement from salts, 452-455.
 - heat of ionization, 72-73.
 - heat of neutralization, 71-72.
 - ionization, 299-300, 306, 349-351, 439-440.
 - titration, electrometric, 383.
 - titration, indicators, 459-462.
- Acid salts, ionization, 451-452.
- Activity and activity coefficient,
 - change with concentration, 313-315, 442-444.
 - concept, 277-279.
 - determination, 281-285, 361-362, 372, 441-442, 468.
 - relation to
 - electromotive force, 361-362, 372.
 - free energy, 277-279.
 - freezing-point lowering, 281.
 - solubility, 468.
 - vapor-pressure, 280-283.
 - standard states of reference for, 279-285.
- Adiabatic expansion, 111-112, 173, 196-197.
- Aggregation states, 32.
- Alloys,
 - annealing and tempering, 503.
 - compound formation, 497, 505.
 - cooling-curves, 494, 496.
 - diagrams, 496-497, 505, 507.
 - freezing-point lowering, 232, 237, 495.
 - solid solutions, 503-506.
 - ternary, 507-508.
- Annealing, 503.
- Arc process of nitrogen fixation, 422, 473.
- Arrhenius equation, 426.
- Association, molecular, 193, 232-233, 263.
- Atomic and molecular theories,
 - gaseous state, 141-183, 190-195.
 - general discussion, 14-16.
 - liquid state, 208-213, 217-218, 248-249.
 - (See also Electronic and Ionic theories.)
- Atomic weights,
 - determination, 21-23, 131-134, 175.
 - relation to combining weights, 21, 131-132.
 - table of values, 24.
- Avogadro's law, 128.
- BASES. See Acids and Bases.
- Boiling-point
 - composition diagrams, 500-502.
 - concentrated solutions, 256-268, 500-502.
 - constants, determination, 225.
 - raising, relation to
 - composition, 223, 227-229.
 - vapor-pressure, 220-223, 227-229.
 - relation to
 - barometric pressure, 208.
 - heat of vaporization, 119, 207.
 - vapor-pressure, 205-207, 220-223.
- Boyle's law,
 - derivation, 145.
 - statement, 35-36.
- Buffer solutions, 454-455.
- CATALYSIS and catalysts,
 - contact, 421.
 - enzymes, 414-416.
 - hydrogen-ion and hydroxide ion, 412-414.
 - mechanism, 412, 415, 418-420.
 - solvents, 487.

Cells, voltaic. See Voltaic cells.

Chemical

formulas, 25-26.

principles, 1.

substances

classes, 11-13, 26.

relation to Henry's law, 248-249.

relation to Raoult's law, 217.

Clapeyron equation,

derivation, kinetic, 211-213.

derivation, thermodynamic, 117-119, 121.

formulation, 119, 207.

integration, 119, 207.

Clark standard cell, 376.

Cohesion of gases, 193, 198.

Color-change of indicators, 455, 457.

Combining volume of gases, 127.

Combining weights,

determination, 21-23.

law, 14.

Complex-salt formation, 250, 254, 300, 336, 382, 467, 469, 509.

Components,

concept, 38, 478.

determination, 479-480.

(See Phase equilibria.)

Composition by weight, 13-16, 21-28, 200-201.

Compound formation

in alloys, 497, 505.

in solutions, 263.

Compression of liquids, 99.

Concentrated solutions, 232-244.

Concentration,

by hot gases, 79.

cells, 362-363.

classification, 200-203.

polarization, 387-388.

Concepts, properties, fundamental constants,

absolute temperature, 36, 113.

acid-exponent, 454.

acidity, 454.

activity, 277.

activity-coefficient, 280, 282, 284, 361.

adiabatic process, 54.

aggregation states (colloid, dispersed, dissolved, gaseous, liquid, solid, amorphous, solid crystalline), 32.

ampere, 321.

anion, 298.

anode, 316.

Concepts, properties, fundamental constants (continued)

atmosphere, 31.

atom, 15.

atom, nucleus, 18.

atomic number, 18, 25.

atomic weight, 15.

attraction pressure, 193.

Avogadro's number, 129.

base-exponent, 454.

bivariant, 42.

boiling-point, 41, 207.

boiling-point, molal raising, 224.

boiling-point, mol-ratio raising, 224.

Boltzmann's constant, 128, 147.

buffer solutions, 454.

catalysis, 412.

cathode, 316.

cation, 298.

centigrade degree, 31.

change in state of a system, 46.

chemical change, 1.

chemical formula, 25.

chemical kinetics, 397.

chemical potential, 286, 291.

chemical principles, 1, 2.

chemical species, 26.

chemistry, 1, 2.

cohesion-pressure, 193.

combining weight, 14.

component, 38, 478.

compound substance, 13.

compression-coefficient, 34.

concentrated solutions, 200.

concentration, 200-203.

concentration-cell, 362.

conductance, actual, 338.

conductance, equivalent, 338.

conductance, ratio, 346.

conductance, specific, 338.

contact-catalysis, 421.

cooling-curves, 494.

coulomb, 321.

critical pressure, 43.

critical temperature, 43.

current-density, 387.

cycle of changes, 80.

decomposition potential, 388.

density, 30.

deviation-coefficient, 261.

dielectric constant, 301.

dissociation, 435.

dissociation-constant, 435.

dissociation pressure, 465.

distribution-constant, 247.

distribution-ratio, 253.

effusion, 148.

Concepts, properties, fundamental constants (continued)

elastic collision, 141.
 electrode, 316.
 electrode-potential, 364, 366.
 electrode-potential, molal, 317, 367.
 electrolyte, 316.
 electrolysis, 316.
 electromotive force, 89.
 electron, 17.
 electron-charge, 17.
 electron, mass, 17.
 electronic equation, 324.
 electronic theory, 17.
 electrovalence, 298.
 element, 13.
 elementary substance, 13.
 energy, 44, 45-46.
 energy-content, 46.
 energy-efficiency, 392.
 energy forms classed as work (chemical, compression, electrostatic, gravitational, kinetic), 47.
 energy of activation, 429.
 entropy, 114.
 entropy, absolute, 527.
 enzyme, 414.
 equation of state, 33.
 equilibrium, 39.
 equilibrium-constant, 286-289.
 equivalent
 electrochemical, 321.
 metathetic, 28.
 oxidation, 28.
 weight, 27-28.
 eutectic mixture, 494.
 eutectic point, 494.
 eutectic, ternary, 508.
 expansion-coefficient, 34.
 faraday, 89, 321.
 force, 31.
 force of gravity, 31.
 formal concentration, volume-formality, 201.
 weight-formality, 201.
 formular values, 29.
 formular weight, 27.
 fractionation, 11.
 free energy, 96, 115.
 free path, mean, 151.
 freezing-point, 41, 230.
 freezing-point, molal raising, 231.
 freezing-point, mol-ratio raising, 231.
 fugacity, 280, 283.
 gas-constant, 35.

Concepts, properties, fundamental constants (continued)

gas, perfect, 35, 63.
 gas-polarization, 389.
 heat, 44, 47.
 heat-capacity, 53.
 heat-capacity, molar, 53.
 heat-capacity-ratio, 171.
 heat-capacity, specific, 53.
 heat-content, 57.
 heat of
 dilution, 70, 269.
 partial, 274.
 formation, 67.
 fusion, 59.
 reaction, 64.
 solution, 69-70.
 partial, 274.
 transition, 59.
 vaporization, 59.
 heat, mechanical equivalent of, 31.
 humidity, 491.
 hydrate, 248.
 hydration, 233.
 hydrogen-ion-exponent, pH , 381.
 hydrolysis, 445.
 hydrolysis-constant, 447.
 indicator, neutralization, 455.
 indicator-constant, 456.
 indicator-exponent, 457.
 ion, 96, 298.
 ion-atmosphere, 302.
 ion-attraction theory, 300.
 ion-conductance, 342.
 ionic-strength, 304.
 ionic theory, 297-298.
 ionization, 299.
 ionization-constant, 439.
 ion-molecule, 324.
 irreversible process, 84.
 isochore, 186.
 isotherm, 184.
 isothermal process, 54.
 Joule-Thomson coefficient, 196.
 kinetic theory,
 fundamental hypothesis, 141.
 pressure hypothesis, 141.
 temperature theorem, 141.
 liquid-potential, 364.
 mass, 9-10.
 matter, 9-10.
 melting-point, 41.
 mixture, 12.
 mobility of ions, 329.
 mol, 27, 37, 103.

Concepts, properties, fundamental constants (continued)

molal concentration,
 volume-molality, 201.
 weight-molality, 201.
 molar-coefficient, 297.
 molar values, 29.
 molar weight, 27.
 molecular
 formula, 25.
 species, 26.
 weight, 27.
 molecule, 15.
 mol-fraction, 137.
 mol-molecule number, 129.
 moment of inertia, 178.
 momentum, 9, 31, 45.
 neutron, 17.
 normal concentration,
 volume-normality, 201.
 weight-normality, 201.
 normal liquid or vapor, 193.
 nucleus of atom, 18.
 osmotic pressure, 238.
 overvoltage, 390.
 partial molar quantities, 272.
 partial pressure, 136.
 perpetual motion,
 first kind, 45.
 second kind, 80.
 phase, 38.
 physical change, 1.
 physical chemistry, 1-2.
 physical properties,
 extensive, 29.
 intensive, 29.
 molar, 29.
 specific, 29.
 physical sciences, 2.
 physics, 1.
 Planck's constant, 179.
 polarization, 387.
 positron, 17.
 pressure, 30.
 probability-function, 162.
 process, 46.
 proton, 17.
 proton-charge, 17.
 proton mass, 17.
 pure substance, 12.
 quantum, 179.
 quantum mechanics, 179.
 quantum number, 179.
 quantum state, 180.
 reaction,
 homogeneous, 397.
 mechanism, 398.
 order, 401.

Concepts, properties, fundamental constants (continued)

reaction,
 rate, 397.
 specific reaction-rate, 398.
 uni-, bi-, tri-molecular, 405.
 reactive molecules, 429.
 reduction-potential, 366.
 resistance, 338.
 reversible process, 81-84, 111.
 salt-error, 458.
 salting-out effect, 250.
 semi-permeable wall, 136, 238.
 solubility, 247.
 solubility-product, 468.
 solute, 200.
 solutions,
 concentrated, 200.
 dilute, 200.
 ideal, 259.
 perfect, 203.
 Raoult law, 217.
 solid, 230, 503.
 solvate, 248.
 solvation, 233.
 solvent, 200.
 standard state of unit-activity,
 gaseous constituent,
 283-285.
 solute, 281-282.
 solvent, 280.
 steady state, 208.
 stoichiometric quantity, 27.
 strength of acid or base, 452.
 strong electrolyte, 340.
 substrate, 415.
 surroundings, 47.
 system,
 definition, 38, 46.
 heterogeneous, 38.
 homogeneous, 38.
 state of, 46.
 temperature,
 absolute, 36.
 centigrade, 31, 36.
 thermodynamic - (Kelvin),
 113.
 thermal pressure, 193.
 thermochemistry, 64.
 thermodynamics, 47.
 transference, 326.
 transference-number, 327.
 transition-point, 41, 485.
 transition-pressure, 41, 485.
 triple-point, 41, 485.
 univariant, 42.
 universal constant, 35.
 van der Waals' constants, 185, 189.

- Concepts, properties, fundamental constants (continued)
 vapor-pressure, 41, 205.
 variance, 42.
 velocity of molecules,
 average or mean, 142, 167.
 most probable, 167.
 root-mean-square, 142, 148, 166.
 viscosity-coefficient, 158.
 voltaic-action, 316.
 voltaic cell, 85.
 weight, 9-10.
 work, 47.
 work-content, 95, 115.
- Conductance, electrical
 actual, specific, equivalent, 338.
 concentration, change with, 339-341.
 determination, 339.
 equivalent, at zero concentration, 340.
 ion-, determination and values, 342-344.
 ion-concentration, determination, 348-349.
 relation to
 concentration and ion-mobility, 345-346.
 ion-attraction, 351-354.
 ionization, 346, 349-351.
 transference, 342-343.
 viscosity, 346.
- Conduction,
 electrolytic,
 Faraday's law, 89, 321.
 general discussion, 316.
 mechanism, 322-323, 328-330.
 metallic, 316, 322.
- Conservation law
 of elements, 13.
 of energy, 44.
 of matter, 10.
- Constants of chemical substances, activity-coefficients of ions, 443.
 atomic weights, 24.
 boiling-point constants for solvents, 225.
 coefficients in the conductance-concentration function for salts, 341, 354.
 composition of air, 138.
 conductance ratios for strong electrolytes, 347, 441.
 density of
 air, 38.
 mercury, 31.
- Constants of chemical substances (continued)
 deviation-coefficients
 for concentrated solutions, 260.
 for gases at 0°, 134.
 electrode-potentials, molal, 318, 371.
 equivalent conductance of strong electrolytes, 340.
 freezing-point constant for solvents, 232.
 heat-capacities of
 gases, 75, 174.
 mercuric oxide, at low temperatures, 528.
 mercury, liquid, 525.
 mercury, solid at low temperatures, 524.
 heats of vaporization, normal liquids, 214.
 hydration of ions, 337.
 indicator constants,
 pH range for color change, 457.
 pK_i, at different ionic strengths, 457.
 ion-conductances, 344.
 ionization-constants of
 acids and bases, 439.
 polybasic acids, 450.
 water, 445.
 molal weight of air, 37.
 molar-coefficients of salts, 298.
 molar entropies of gases, 530, 533, 534.
 molar free energies,
 absolute, 534.
 standard, 517, 518.
 molar heat-contents,
 absolute, 533.
 standard, 517.
 molecular magnitudes, 160.
 overvoltages, 391.
 pressure-volume product of gases,
 at high pressure, 184, 188.
 at moderate pressure, 134.
 solubilities of air-gases, 250.
 transference numbers, 334.
 van der Waals' constants, 188.
- Cooling-curves, 494, 495.
- DALTON's partial pressure law, 137.
 Decomposition-potential, 388.
 Definite proportions, law, 13.
 Dehydration. See Drying.
 Diagrams. See Phase diagrams.

- Diffusion-potentials. See Liquid-potentials.
- Dilution, heat of, 70, 269, 274.
- Displacement of acids and bases, 452-454.
- Dissociation of gases,
determination from density, 139-140, 435-436.
mass-action relations, 435-438.
pressure, effect of, 437.
- Dissociation of solids,
dissociation-pressure, 92, 465, 473, 488-489.
gas phase with one component, 488-492.
gas phase with two components, 465.
gaseous and liquid phases, 509.
- Distillation,
fractional, 256-259, 500-503.
steam, 206.
- Distribution of
base between acids, 452-454.
kinetic energies, 161-167, 182-183.
molecular velocities, 161-167.
molecules in field of force, 167-170.
solutes between phases, 247-250, 253-255.
- Dry cell, 376.
- Drying of
organic liquids, 492.
salt hydrates, 491.
- EFFLORESCENCE of salt-hydrates, 491.
- Effusion of gases, 149-151.
- Electro-analysis, 388-389.
- Electrode-potentials,
concentration effect, 368-370.
determination, 370-374.
mechanism, 364-365.
molal, 317, 366-369.
molal hydrogen, 370.
normal calomel cell, 373.
relation to equilibrium of oxidation reactions, 384-386.
temperature effect, 394.
- Electrolysis,
deposition of metals, 388.
energy-efficiency, 392.
Faraday's law, 89, 321.
formulation of electronic reactions, 323-325.
mechanism, 322-323.
polarization, 388-392.
products, 319.
separation of elements, 389.
- Electrometric titration, 383.
- Electromotive force,
back, determination, 390-391.
cells involving
chemical changes, 90, 359-360.
concentrated solutions, 375-376.
physical changes, 85-90, 362-363.
concentration cells, 362-363.
relation to
activity and activity coefficients, 361-362.
concentration, 361-362, 387.
electrode-potentials, 364-365, 375.
equilibrium-constant, 360.
free energy, 102, 355.
temperature, 393.
- Electronic theory, structure of atoms, 17-19.
- Elements and elementary substances,
general relations, 13.
molecular forms of gaseous, 136.
separation by electrolysis, 389.
- Energy,
conservation, 44.
content in general, 46-48, 56-61.
content of
imperfect gases, 196-199.
perfect gases, 61-63.
general discussion, 44-50.
molecular, 176-183.
of activation, 429.
- Entropy,
changes attending
chemical changes, 527-529.
physical changes, 116-117.
concept, 113-116.
content,
general discussion, 523-527.
perfect gases,
monatomic, 529-530.
polyatomic, 531-535.
- Enzymes, 414-416.
- Equations,
electronic, 323-325.
entropy, 523.
free energy, 279, 292, 367, 512.
heat-content, 64-69, 274.
of state
of gases, 35, 133, 185, 190, 284.
of liquids, 33, 267.
- Equilibrium of gas or solute reactions,
derivation from free energy, 289-295.

- Equilibrium of gas or solute reactions**
(continued)
derivation from reaction-rate, 408-409.
general discussion, 286-296, 433-434, 463-464.
oxidation-reactions, 384-386.
relation to
electromotive force, 360.
free energy, 289-295.
pressure, 437.
temperature, 471-475.
(See also Mass-action law, and Phase equilibria.)
- Equilibrium of polyphase systems,**
general considerations, 40-43, 100-101, 103-104, 509-510.
phase-rule, 476-483.
relation to
molar free energy, 480-483.
pressure and temperature, 117-121.
systems with
one component, 484-487.
solid solutions, 503-506.
three components, 507-510.
two components, 488-506.
unstable conditions, 485-487, 498-499.
(See also Phase diagrams and Phase rule.)
- Equilibrium-constants, relation to**
dissociation-constants, 437.
electrode-potentials, 385-386.
electromotive force, 360, 382, 384-386.
free energies, 289-296, 511-522.
ionization-constants, 448-449.
reaction-rate, 407-409.
- Eutectic,**
composition, 494-496.
point, 494, 508.
texture, 494.
- Explosions, pressure and temperature,**
78.
- Extraction by solvents,** 254.
- FARADAY's law,** 89, 321.
- Flames, maximum temperature,** 78.
- Formation,**
free energy of, 511-513.
heat of, 66-69, 511-513.
- Free energy**
activity, relation to, 277-278.
change attending
activity changes, 278.
- Free energy (continued)**
change attending
chemical changes, 101-103, 289-294.
compression of liquids, 99.
concentration changes, 269-271, 361-362.
expansion of gases, 98-99.
formation of compounds, 514-517.
transfer between phases, 514.
transfer between solutions, 269-271.
transition of unstable phases, 99, 486, 514, 515.
voltaic action, 102, 271, 355-380.
volume changes, 98-100.
concept, 94-98, 115.
electromotive force, relation to, 102, 271, 355-380.
equilibrium, relation to, 101, 289-296.
ions, 512.
of formation, 511-513.
partial molar, 272-273, 277-279, 512-519.
standard, 294, 512.
substances, 278-279, 511-519.
temperature, effect of, 116, 122-124, 515.
values,
from equilibrium data, 513-517.
from heat data, 527-529.
from spectroscopic data, 531-535.
tabulation of, 517-518, 534.
- Freezing-point,**
constants, 231-232.
heat of fusion, relation to, 235-236.
lowering, composition relations, 231, 235-236.
lowering, effect of strong electrolytes, 297-299, 306.
lowering of metals, 232, 237, 495.
pressure, effect of, 120, 485.
raising by solutes, 503-504.
solid solutions, 503-505.
vapor-pressure relations, 234-236.
- Functional notation,** 33.
- GAS-CONSTANT, evaluation,** 35.
- Gases,**
cohesion, 193, 198.

Gases (continued)

- dissociation, 140, 435-436.
- effusion, 149.
- energy of imperfect, 196-198.
- energy of perfect, 61-62.
- entropy of perfect, 525, 529-535.
- kinetic theory, 141-170, 176-183, 190-195.
- mass-action relations, 435-438, 465-466.
- partial-pressure, 137-138.
- reactions,
 - equilibrium, temperature-effect, 471-473.
 - heat of, 54-56, 64-66.
 - rate of, 421-425.
- solubility, 247-250.
- volume
 - at high pressures, 184-195.
 - at moderate pressures, 133-134.
 - of perfect, 127-129, 136-137, 144-145.

Gibbs-Helmholtz equation, 393.

HEAT of fusion, relation to, freezing-point lowering, 231, 235.
heats of sublimation and vaporization, 235.

Heat of reaction of various types.
See Heat-content increase.

Heat of Vaporization. See Vaporization.

Heat-capacity,
general discussion, 52-54.
influence on heat of reaction, 73-77.

- of perfect gases,
 - determination, 53, 171-173.
 - kinetic interpretation, 176-183.
 - relation to atomic weight, 175-176.
 - relation to molecular complexity, 173-175.
 - ratio for gases, 171-172.
 - solids at low temperatures, 524, 526, 528.

Heat-content increase attending aqueous-solution reactions, 71-73.
dilution, 69-71, 269, 274.
formation of compounds, 66-69, 511-513.
gaseous reactions, 56.
ionization, 72-73.
neutralization, 71-72.
solution, 69-71, 274.
transition, 70.

Henry's law, 247-250.

Hydrates of salts. See Salt-hydrates.

Hydration of
ions, 337, 344.
solutes, 248-249, 446.

Hydrogen-ion,
catalytic effect, 412-415.
concentration
change on neutralization, 459-460.
determination, 382, 411-412, 458.

in water, 349.

Hydrogen-exponent, 381.

Hydrolysis of salts,
constant, 447-449.
determination, 446-447.
mass-action relations, 445-449.
temperature-effect, 475.

Hygrosopicity of salts, 491.

INDICATORS,

color changes, 457.

constants,
determination, 458.
values, 457.

principles, 455-457.

use of in
acid-base titrations, 459-462.
determination of pH , 458.

Ion-attraction theory,

basis of, 300-303.

derivation of equations, 307-315.

relation to

mass-action effects of ions,
313-315.

mobility of ions, 351-354.

molar effects of ions, 303-306, 313.

validity of, 306-307.

Ionic theory, explanation of conductance, 342-346.

electrode-potentials, 364-365.

electrolysis, 323-325.

electromotive force, 364-365.

heat of reaction, 72-73.

largely ionized substances, 347-348.

liquid-potentials, 365-366.

mass-action effects, 439-462, 466-470.

molar properties, 297-299.

reaction-rate, 399.

transference, 328-330.

voltaic action, 355-359.

Ions or ion-constituents,
 activity and activity-coefficient,
 313-315, 361-362, 371-
 372, 441-444.
 complex, 250, 254, 300, 336, 382.
 concentration, determined by
 conductance, 349.
 electromotive force, 380-383.
 conductance, 342-344.
 electric charge on, 323.
 free energy, 513.
 hydration, 337, 344.
 mobility. *See* Mobility, ionic.
 transference, 328-331.

Ionization,
 acids and bases, 349-350, 439-
 440.
 acid salts, 451-452.
 common-ion effect, 440.
 dibasic acids, 449-452.
 from conductance, 349-350, 439.
 from molar-coefficients, 299, 306.
 general discussion, 297-300, 328-
 329, 347-350, 439-441.
 heat of, 73.
 mass-action relations, 439-445.
 salts, 440-441.
 water, 349, 444-445.
Ionization-constants,
 acids and bases, 439.
 determination, 439-440, 449,
 451-452, 458-459.
 polybasic acids, 450.
 water, 445.

Irreversible processes, 84.

JOULE-Thomson coefficient, 196.

KINETIC

derivation of,
 Clapeyron equation, 213.
 expression for vapor-pres-
 sure and heat of vapori-
 zation, 211-212.
 perfect gas laws, 144-145.
 pressure of perfect gas, 143-
 144.
 van der Waals' equation,
 190-192.
 energies of molecules, 147, 161-
 166, 176-183.
 hypotheses, 141-142.
 interpretation of deviations from
 energy-content law of per-
 fect gases, 198.
 Raoult's law, 266-268.
 van der Waals' equation,
 193.

KINETIC (continued)

interpretation of
 effusion of gases, 149-150.
 heat-capacity of gases, 176-
 183.
 Raoult's law, 217-218.
 reaction-rate, temperature
 effect, 429-432.
 vaporization, 208-210.
 viscosity of gases, 158-159.

LAWS, principles, fundamental equa- tions,

Arrhenius equation, 426.
 Avogadro's, 128.
 boiling point raising for
 perfect solutions, 223.
 Raoult law solutions, 223,
 229.
 Boltzmann's equation, 168.
 Boyle's, 35-36.
 Carnot's, 108.
 Charles', temperature effect, 36.
 Clapeyron equation,
 approximate, 119, 207.
 exact, 119, 207.
 combining volumes, 127.
 combining weights, 14.
 conductance-concentration func-
 tion for salts, 340.
 conservation of
 elements, 13.
 energy, 44.
 matter, 10.
 Coulomb's, 301.
 Dalton's partial pressure, 137.
 definite
 properties of pure sub-
 stances, 13.
 proportions, 13.
 distribution between phases, 253.
 Duhem equation, 251, 276.
 electrode-potential equation, 369.
 energy-content of perfect gases,
 61.
 equipartition of energy, 177.
 Faraday's, 89, 321.
 first law equation, 48.
 freezing-point lowering for
 perfect solutions, 231.
 Raoult law solutions, 231,
 236.
 gases
 at moderate pressure, 133.
 perfect, 34-36, 61, 127-128.
 Gibbs-Helmholtz equation, 393.
 Gay-Lussac's, temperature effect,
 36.

LAWs, principles, fundamental equations (continued)

heat of reaction, temperature effect, 60, 74.

Henry's, 247.

Hildebrand's rule, 214.

Hittorf's transference, 328.

independence of reaction-rates, 406.

independent migration of ions, 343.

indicator equation, 456.

initial and final states, 46.

ion-attraction equations,
activity-coefficient, 313-315.
mobility and conductance,
352-353.

molar-coefficient, 303-304.

osmotic pressure, 313.

Joule's, 88.

Kinetic equation for

collision-frequency, 153.

collision-rate, molecules of
two kinds, 156.

distribution of
rotational energies be-
tween quantum
states, 185.

translational energies,
163, 165-166.

velocities, 163, 165-166.

effective volume, 155.

effusion-rate, 149.

energy of vaporization, 210,
213.

imperfect gases, 192.

mean free-path, 153, 154.

perfect gases, 143.

quantum of rotational en-
ergy, 155.

vapor-pressure, 213.

viscosity, 159.

liquid-potential equations, 377-
378.

mass-action law of equilibrium,
286-288.

mass-action law of reaction rate,
379.

Maxwell's distribution, 162.

Nernst heat theorem, 527.

Ohm's, 338.

osmotic pressure, 240, 242-244.

partial molar quantities,
relation between, in a two-
component system, 275.

summation law, 272.

perfect solutions, 216.

perpetual motion principle, 80.

LAWs, principles, fundamental equations (continued)

phase rule, 476.

Raoult's, 216, 218.

relativity principle of Einstein,
11.

Sackur equation, 530.

second law equation, 109.

second law free energy equation,
122, 124.

solubility of gases, 247.

solubility-product, 468.

solvent-solubility lowering, 255.

Stokes', 20.

thermodynamics,

first law, 48.

second law, 105, 114-115.

third law, 527.

Trouton's rule, 214.

van der Waals' equation, 185,
192.

van't Hoff equation, 471.

Liquids,

boiling-point, 207.

compression of, 99.

heat of mixing, 264, 265-266.

heat of vaporization, 210, 214-
215.

partially miscible, 206, 255, 259,
499-500.

pressure, effect on vapor-pres-
sure, 245.

vapor-pressure, 41, 205-213, 220-
224, 234-236, 242-246.

volume change on mixing, 264,
265-266.

Liquid-potentials,

conventions, 365.

derivation of equations, 377, 379.

equations for, 377-378.

relation to ionic theory, 365-366.

relation to thermodynamics, 376-
380.

Liquefaction temperatures of gases,

194.

MASS-ACTION law of equilibrium,

applied to

equilibrium in general, 286-
296, 433-434, 463-464.

gas reactions, 435-438.

indicators, 455-462.

oxidation-reactions, 384-
386.

solids and gases, 465-466.

solids and solutes, 466-470.

solute reactions, 439-462.

derivation, 289-295, 408-409.

- MASS-ACTION** law of equilibrium (continued)
formulation, 286-288, 295, 463-464.
phase rule, contrasted, 509-510.
- Mass-action** law of reaction-rate, 397-398.
- Maxwell's** distribution law, 162.
- Melting-point.** See **Freezing-point.**
- Metals,**
deposition by electrolysis, 388.
polarization, 391-392.
(See also **Alloys.**)
- Molar-coefficients** of salts and ions,
concept, 297.
relation to ion-attraction, 303-306, 313.
table of values, 298.
- Molar free energy,**
concept, 273.
effect of temperature, 116, 123.
standard values, 517-518, 534.
- Mobility** of ions,
conductance, relation to, 345-346.
determination of, 330-333.
general discussion, 328-330.
ion-attraction, effect of, 351-354.
transference, relation to, 328-330.
viscosity, effect of, 346.
- Molecular**
formulas, 25-26.
formulas of
dissolved substances, 233.
gaseous substances, 135-136.
metals in mercury, 220.
interpretation of reaction-rate,
temperature effect, 432.
magnitudes, 159-161, 193-195.
mechanism of electromotive
force, 364-366.
mechanism of reactions, 397-400,
405, 412, 415, 417-420.
species, 26.
weight
of gases, 129-131, 150-151.
of solutes, 226, 232.
(See also **Molecules** and **Kinetic.**)
- Molecules,**
attraction, 190-193.
collisions with one another, 151-157.
diameter, significance, 155-166.
distribution in field of force, 167-170.
distribution of energies and velocities, 161-167.
- Molecules** (continued)
free path, 151-154.
impacts on unit surface, 148.
kinetic energies, 147, 176.
number in one mol, 145.
rotational energy, quantization,
179-183.
velocity, 142, 148, 166-167.
volume, effective, 155, 191.
- Moving-boundary** method of transference, 331-334.
- NERNST** heat-theorem, 527.
- Neutralization-indicators,**
application to
acid-base titrations, 459-462.
determination of pH , 458.
mass-action relations, 455-459.
- Nitrogen-fixation,** arc process, 422-423.
- OHM's** law, 338.
- Order** of reactions, 400-403.
- Osmotic pressure,**
experimental determination, 239-240.
general discussion, 238-239.
relation to
composition, 240, 243.
free energy, 241.
hydrostatic pressure, 240.
vapor-pressure, 242-243.
- Overvoltage,** 389-392.
- Oxidation-reactions,**
equilibrium in relation to electrode-potentials, 384-386.
- PARTIAL** molar quantities,
concept, 272.
evaluation of, 273-274.
relation to Duhem equation, 276.
relations in a two-component system, 275.
summation law, 272.
- Perpetual motion,**
first kind, 45.
phase-equilibrium derivation,
103-104.
second kind, 80.
- Phase diagrams,**
freezing-point composition, for
Raoult law solutions,
237.
pressure-composition, 256-259,
500, 502-503.
pressure-temperature, 42-43,
484-486, 488-491.

Phase diagrams (continued)

- substances,
 - acetic-acid benzene, 493-495.
 - alloys, 496-497, 503-506.
 - organic liquids, 256-259, 500-503.
 - salt hydrates, 489-492, 497-499.
 - sulfur, 484-486.
 - water, 42, 486.
 - water succinonitrile, 499-500.
- temperature-composition, 492-503.
- triangular, 507.
- vapor-pressure composition, 256-259.
- vapor-pressure temperature,
 - for boiling-point, 221.
 - for freezing-point, 234.

Phase rule,

- component-concept, 38, 478-480.
- derivation deductively, 480-483.
- derivation inductively, 477.
- mass-action law contrasted, 509-510.
- statement, 476.
- variance-concept, 42.

Polarization,

- concentration, 387.
- gas, 389.

Porous plug experiment, 196.**Pressure of gases,**

- cohesion, 193.
- height, change with, 168.
- kinetic interpretation, 141-144, 190-193.
- partial, 136-138.
- thermal, 193.
- volume and temperature relations, 127, 133-134, 184-190.
- wet and dry, 205.

Probability of kinetic energies, 161-165.**Producer-gas process, 138, 466.****QUINHYDRONE electrode, 372.****RAOULT's law,**

- corrected for imperfect vapor, 218.
- deviations,
 - determination, 256.
 - interpretation, 261-263.
 - magnitude of, 259-261.
 - related properties, 263-268.

RAOULT's law (continued)

- kinetic interpretation, 217.
- verification, 219.

Rate of reactions,

- catalytic effects,
 - enzymes, 415.
 - hydrogen-ion, 412-413.
 - oxidation reactions, 418-420.
- enzyme, 414-416.
- homogeneous,
 - dissolved substances, 410-420.
 - gaseous substances, 421-425.
 - general considerations, 397-409.
 - mass-action law, 397-400.
 - mechanism, 398-399, 404-405.
 - order of reaction, 400-403.
 - oxidation, 416-420.
- hydrolytic, 410-414.

simultaneous,

- consecutive, 405-406.
- independent, 405-406.
- opposing, 407-409.

temperature effect,

- energy interpretation, 429-431.
- general principles, 426-427.
- molecular interpretation, 432.
- relation to equilibrium, 427-429.

Reduction-potentials, 366-369.**Reversible processes, 84-92, 110-111.****SALT-hydrates,**

- dehydration of organic liquids, 492.
- determination of existing, 491, 498.
- diagrams, 490-492, 497-499.
- drying, 491.
- efflorescence and hygroscopicity, 491.
- preparation, 498.
- solubility, 497-499.
- transition, 491, 498.
- unstable forms, 498-499.
- vapor-pressures, 489-492.

Salting-in by ion-attraction, 468.**Salting-out effect, 250, 283.****Salts. See Substances, strong electrolytes.****Semi-permeable walls, 136, 238.****Shaking-out by solvents, 254.****Solid solutions, 503-506.**

Solubility of

- gases, 247-250.
- salts, determined from
 - conductance, 349.
 - electromotive force, 382.
- solvents in one another, 255.
- strong electrolytes, effect of
 - common-ion, 469.
 - complex-formation, 469.
 - ion-attraction, 468.
 - metathesis, 469-470.
 - temperature, 475.
 - unionized and slightly ionized substances, 466-467.
 - unstable phases, 486, 498.

Solution, heat of, 69-70, 72, 475.

Solutions (and solutes),

- boiling-point relations, 220-229.
- classes, 200, 203, 217, 259.
- composition, expression of, 200-203.
- conductance, 338-354.
- electrolysis, 316-325, 388-392.
- energy relations, 269-285.
- freezing-point relations, 230-237.
- osmotic pressure relations, 238-246.
- Raoult's law deviations, 256-268.
- reactions,
 - equilibrium of. See Equilibrium.
 - rate of. See Rate of reactions.
- solid, 503-506.
- solute distribution between phases, 253-255.
- solute vapor-pressure, 247-252.
- solvent vapor-pressure, 220-229.
- thermochemistry of, 71-73.
- transference, 326-337.

Specific heat. See Heat-capacity.

Standard cell, Clark, 376.

Standard states of unit-activity, 279-285.

Steam distillation, 206.

Storage cells, 358-359, 376.

Substances,

- chemical classes, 13, 26.
- slightly ionized (weak electrolytes),
 - conductance at zero concentration, 349-350.
 - ionization, 349-351, 439-440.
- (See Acids and bases.)
- strong electrolytes,
 - activity-coefficients, 443.

Substances (continued)

- strong electrolytes,
 - conductance, 339-342.
 - heat of reactions, 71-73.
 - ionization, 347-348, 440-441.
 - solubility, 467-470.

TEMPERATURE-change produced by
adiabatic expansion of gases, 173, 196-197.

flames and explosions, 78.

mixing of liquids, 264.

Temperature-composition diagrams.
See Phase diagrams.

Tempering, 503.

Thermochemistry,

- application of principles, 77-79.
- heat of reaction,
 - definition, 64.
 - effect of temperature, 73-77.
 - from heats of formation, 66-69.
 - in aqueous solution, 71-73.
- heat-content equations, 64-66.
- heats of solution and dilution, 69-71.

Thermodynamics,

- definition, 47.
- first law, 48.
- relations at absolute zero, 526-527.
- second law, 80, 94, 105-109, 112, 113-116.
- third law, 526-527.

Transference (electrical)

- concentration, effect of, 334-336.
- conductance, relation to, 328-330.
- determination of
 - composition of ions, 336.
 - hydration of ions, 336-337.
- general discussion, 326.
- ion-mobility, relation to, 328-330.
- mechanism, 328-329.
- methods of determination,
 - electromotive force, 363.
 - Hittorf, 327.
 - moving boundary, 331-334.
- number,
 - definition, 327.
 - Hittorf, 337.
 - true, 337.

Transition,

- catalysis of, 487.
- free energy of, 486, 514, 515.
- heat of, 70.
- salt hydrates, 491.
- temperature, determination, 487.

Transition (continued)
 temperature, effect of pressure,
 120, 485.

Trouton's rule, 214.

UNITS, definitions,
 ampere, 321.
 atmosphere, 31.
 bar, 30.
 calorie, 31.
 coulomb, 321.
 degree centigrade, 31.
 dyne, 31.
 erg, 31.
 faraday, 321.
 joule, 31.
 megabar, 31.
 mho, 338.
 mol, 37.
 ohm, 338.
 reciprocal ohm, 338.

Univariant systems, temperature-
 pressure relations, 120-
 121.

VAN DER WAALS' equation, 184-185,
 190-193.

van't Hoff equation, 427, 471.

Vapor-density, determination, 129-
 131.

Vapor-pressure,
 composition diagrams, 256-259.
 determination, 205, 256.
 general discussion, 205.
 molecular interpretation, 208-
 213, 217.

of various systems,
 partially miscible, 206, 255.
 perfect solutes, 247-250.
 salt-hydrates, 489-491.
 solutions, concentrated,
 256-268.
 solutions, dilute, 216-220,
 247-250.
 solvents, 216-220.

relation to
 activity, 280-283.
 boiling-point, 220-224, 227.
 composition (Raoult's law),
 216.

Vapor-pressure (continued)
 relation to
 freezing-point, 234-236.
 heat of vaporization, 117-
 119, 207, 210, 213.
 pressure, 245-246.
 temperature, 117-119, 207.

Variance, 42.

Viscosity,
 ion-probability, effect on, 346.
 of gases, 157-159.

Voltaic cells,
 change in state, 355-359.
 concentration cells, 362-363.
 conduction in, 322-325.
 electrode potentials, 364-375.
 electrode products, 319.
 electromotive force, 86-89, 364-
 365.
 formulation, 357.
 free energy decrease, 102, 355.
 liquid-potentials, 365-366, 376-
 380.
 polarization, 387-392.
 work produced, 89, 358.

Voltaic cells involving
 chemical changes, 90-91, 94, 369.
 concentrated solutions, 375-376.
 physical changes, 85-90, 94, 362-
 363.

WORK-content,
 concept, 94-96, 115.
 temperature, effect of, 116, 122-
 124.

work produced by
 expanding a perfect gas at
 constant temperature,
 52.
 heat-transfer between tem-
 peratures, 106-113.
 heating a perfect gas at con-
 stant pressure, 52.
 phase transitions, 52.
 reversible processes, 81-94.
 voltaic cells, 85-90.
 volume-changes in general,
 50-52.

Work, thermodynamic significance
 of, 47-49.

