TIGHT BINDING BOOK

UNIVERSAL
LIBRARY

OU_158150

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 541, G396. Accession No. 16220

Author Getman, Frederick H.

Title Outlines of Theoretical Chemistry.

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

OUTLINES OF THEORETICAL CHEMISTRY

BY

FREDERICK H. GETMAN, Ph.D.

Formerly Associate Professor of Chemistry in Bryn Mawr College

FIFTH EDITION

REVISED AND LARGELY REWRITTEN

BY

FARRINGTON DANIELS

Professor of Chemistry in the University of Wisconsin

NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

1931

COPYRIGHT, 1913, 1918, 1922, 1927
BY FREDERICK H. GETMAN

COPYRIGHT, 1931
BY FREDERICK H. GETMAN AND FARRINGTON DANIELS

All Rights Reserved

This book or any part thereof must not be reproduced in any form without the written permission of the publisher.

Printed in U. S. A.

4-33

Printing
F. H. GILSON CO.
BOSTON

Composition and Plates
TECHNICAL COMPOSITION CO.
CAMBRIDGE

Binding
STANHOPE BINDERY
BOSTON

FOREWORD BY THE SENIOR AUTHOR

The following extract from the preface to the first edition of this text-book has been selected as an appropriate background for the present edition appearing under joint authorship:

> The present book is designed to meet the requirements of classes beginning the study of theoretical, or physical chemistry. A working knowledge of elementary chemistry and physics has been presupposed in the presentation of the subject. . . . With the exception of a few paragraphs in which the application of the calculus is unavoidable, no use is made of the higher mathematics, so that the book should be intelligible to the student of very moderate mathematical attainments.
>
> The contributions to knowledge in the domain of physical chemistry have increased with such rapidity within recent years that the prospective author of a general text-book finds himself confronted with the vexing problem of what to omit rather than what to include. In selecting material for this book, the author has been guided, in large measure, by his own experience in teaching theoretical chemistry to beginners and to advanced students. The attempt has been made to present the more difficult portions of the subject . . . in a clear and logical manner. While the treatment of each topic is necessarily brief, yet the effort has been made to avoid the sacrifice of clearness to brevity.

Since the foregoing words were written, physical chemistry has grown apace, and the problem of presenting a comprehensive outline of the subject within the compass of a text-book of moderate size has become even more difficult of accomplishment than when the author compiled the original text eighteen years ago.

In addition to the rapid development of the science of physical chemistry *per se*, physical science has undergone a veritable cataclysm during this period of eighteen years. Not only has the superstructure been altered, but also many of the basic concepts of physics have been swept away. As Dampier Whetham says,

> In the most striking discoveries of today — those in the theory of atomic structure — the classical laws have broken down, and we are forced to accept the ideas of relativity and quanta. Physical science has successively found many ultimates — gravitating particles, atoms, electrons — and each has gone further and invented models which explained these ultimates in terms of something more fundamental. But in the quantum of "action" and in the equation of the indeterminate particle and wavelet, we see concepts which the mind finds it difficult to picture. Perhaps a new atomic model may be framed successfully once more, but possibly we are approaching fundamental things which cannot be expressed in mechanical terms.

As one considers our present outlook in physical science one is almost inclined to sympathize with Dickens' little old man in faded

black who was so bewildered by the wonders of science seen at Vauxhall Gardens that he exclaimed, "I don't know where this here science is to stop, mind you, that's what bothers me!" Of course we do not mean to imply that science will ever become static, for, as a recent writer has aptly put it:

> Pure science is continually improving and extending our model of nature from the microcosm of the atom to the macrocosm of the visible Universe of spiral nebulae and galaxies of stars. The relations between the older parts of the model are ever becoming better known, and new parts are continually being added, added indeed so fast that there is no time for the adventurous builders to fit them into or even on to, the older structure. When the pace slackens a little, the next generation, like the last, can coördinate and complete the work.

In the meantime, the profound truth of Robert Bridges' recent utterance in his "Testament of Beauty" should be pondered by every student of science —

> Thy task
> is first to learn WHAT IS, and in pursuant knowledge pure intellect
> will find pure pleasur and the only ground for a philosophy conformable to truth.

When the demand for a new edition of this book arose, the author, who for some years has not been actively engaged in teaching, felt very strongly that some one who was not only thoroughly familiar with modern physical chemistry, but also conversant with current pedagogical methods should undertake the task of revision. He considers himself more than fortunate to have enlisted the interest and coöperation of Dr. Farrington Daniels, who for some years has used his text-book with the chemistry classes at the University of Wisconsin. His familiarity with both the merits and defects of the book born of this intimate daily experience in the class-room, together with his outstanding position, both as a teacher and research worker in the field of physical chemistry, eminently qualify Dr. Daniels for the task.

The senior author has left the actual work of revising and rewriting entirely in Dr. Daniels' hands and has acted merely in an editorial and advisory capacity throughout the whole course of revision.

The task of preparing a text-book of physical chemistry for the general student which shall adequately present the science in its present status is by no means an easy one. Not only do we believe that Dr. Daniels has succeeded in bringing the book thoroughly up to date, but we are convinced that he has so skilfully engrafted new material on to old as to preserve, in large measure, the atmosphere of the original text.

It affords the senior author genuine pleasure to record his appreciation of the courtesy and consideration shown him by Dr. Daniels

throughout the progress of the work of revision. He has at all times shown a desire to preserve as much as possible of the original text, and all proposed changes have been submitted to the senior author for his criticism or approval. The most cordial spirit of coöperation has prevailed during the months that the new edition has been in process of preparation, and all suggestions from the senior author have been received with uniform consideration by Dr. Daniels. The present edition, therefore, may be regarded as embodying such material as both authors conceive to be essential to a comprehensive course in modern physical chemistry.

It is our hope, not only that the book in its revised form may be welcomed by its former users, but also that it may win for itself new friends among both teachers and students of chemical science.

FREDERICK H. GETMAN.

STAMFORD, CONN.

PREFACE TO THE FIFTH EDITION

To introduce recent advances without offending old friends who cherish the foundations of a successful past; to keep pace with present tendencies toward the mathematical viewpoint without driving away students who are inadequately prepared; and to sift out the permanent from the trivial are the privileges and responsibilities of this revision.

The first revisions of a book can be made by addition, but there comes a time, as in the present case, when for every addition there must be a corresponding subtraction.

Approximately one-third of the book has been changed. The chapters on Elementary Thermodynamics, Kinetics, Photochemistry and Atomic Structure have been rewritten. The arrangement of chapters has been left unchanged except that two new chapters have been added, one on Chemical Thermodynamics using the notation of G. N. Lewis, and one on an Introduction to Quantum Theory. These fields have now become so important that even elementary students should have some acquaintance with them. The first half of the book has been made simpler, the last half somewhat more advanced. Models and mechanisms have been used freely to help in comprehending new subjects, but they are to be discarded without prejudice when outgrown.

Half of the problems are new. Answers are given for a portion of the problems so that students can check their work and yet not become slaves to answers. Tables and numerical examples have been revised, when possible, to agree with the International Critical Tables.

The new author desires to acknowledge the cordial coöperation of Dr. Getman and the many helpful suggestions which have come from various friends of the book, particularly from Professors J. H. Mathews, N. F. Hall, E. W. Mack, J. C. Van Klooster, J. M. Davey, J. W. Williams, O. W. Browne, O. C. Sloat, and others. He desires especially to thank Mr. Paul C. Cross and Mr. Frank Verhoek for help in proof-reading, and preparation of problems.

FARRINGTON DANIELS.

MADISON, Wis.
May, 1931.

CONTENTS

CHAP.		PAGE
	FOREWORD BY THE SENIOR AUTHOR	iii
	PREFACE TO FIFTH EDITION	vii
I.	FUNDAMENTAL PRINCIPLES	1
II.	GASES	9
III.	LIQUIDS	33
IV.	SOLIDS	62
V.	RELATION BETWEEN PHYSICAL PROPERTIES AND MOLECULAR CONSTITUTION	86
VI.	ELEMENTARY PRINCIPLES OF THERMODYNAMICS	109
VII.	SOLUTIONS	137
VIII.	DILUTE SOLUTIONS AND OSMOTIC PRESSURE	162
IX.	SOLUTIONS OF ELECTROLYTES	193
X.	COLLOIDS	208
XI.	THERMOCHEMISTRY	245
XII.	HOMOGENEOUS EQUILIBRIUM	267
XIII.	HETEROGENEOUS EQUILIBRIUM	288
XIV.	CHEMICAL KINETICS	321
XV.	ELECTRICAL CONDUCTANCE	360
XVI.	ELECTROLYTIC EQUILIBRIUM AND HYDROLYSIS	400
XVII.	ELECTROMOTIVE FORCE	421
XVIII.	ELECTROLYSIS AND POLARIZATION	487
XIX.	CHEMICAL THERMODYNAMICS	506
XX.	PHOTOCHEMISTRY	538
XXI.	ELECTRICAL THEORY OF MATTER	556
XXII.	RADIOACTIVITY	572
XXIII.	ATOMIC STRUCTURE	588
XXIV.	INTRODUCTION TO QUANTUM THEORY	600
	INDEX OF AUTHORS	625
	INDEX OF SUBJECTS	633

OUTLINES OF
THEORETICAL CHEMISTRY

CHAPTER I

FUNDAMENTAL PRINCIPLES

Theoretical Chemistry. That portion of the science of chemistry which has for its object the study of the laws controlling chemical phenomena is called theoretical or physical chemistry. The first attempt to summarize the more important facts and ideas underlying the science of chemistry was made by Dalton in 1808 in his "New System of Chemical Philosophy." The birth of the new science of Theoretical Chemistry may be said to date from the appearance of Dalton's epoch-making book.

Theoretical chemistry is concerned with the great generalizations of chemical science; it aims to systematize all of the established facts of chemistry and to discover the laws governing the various phenomena of chemical action.

Law, Hypothesis, and Theory. The science of chemistry is based upon experimentally established facts. When a number of facts have been collected and classified we may proceed to draw inferences as to the behavior of systems under conditions which have not been investigated. This process of reasoning by analogy we term generalization and the conclusion reached we call a *law*. It is apparent that a law is not an expression of an infallible truth, but it is rather a condensed statement of facts which have been discovered by experiment. It enables us to predict results without recourse to experiment. The fewer the number of cases in which a law has been found to be invalid, the greater becomes our confidence in it, until eventually it may come to be regarded as tantamount to a statement of fact.

Natural laws may be discovered either by the correlation of experimentally determined facts, as outlined above, or by means of a speculation as to the probable cause of the phenomenon in question. Such a speculation in regard to the cause of a phenomenon is called an *hypothesis*.

After an hypothesis has been subjected to the test of experiment and has been shown to apply to a large number of closely related phenomena it is termed a *theory.*

In his address to the British Association (Dundee, 1912), Professor Senier has this to say: " While the method of discovery in chemistry may be described generally, as inductive, still all the modes of inference which have come down to us from Aristotle, analogical, inductive, and deductive, are freely used. An hypothesis is framed which is then tested, directly or indirectly, by observation and experiment. All the skill, and all the resource the inquirer can command, are brought into his service; his work must be accurate; and with unqualified devotion to truth he abides by the result, and the hypothesis is established, and becomes a part of the theory of science, or is rejected or modified."

Most hypotheses are destined to be discarded when new facts and more precise data are obtained, but they fulfil a very necessary function in the development of science. They may be likened to the scaffolding which is used temporarily during the construction of a permanent building. A successful hypothesis is not necessarily a permanent hypothesis, but it is one which stimulates additional research and opens up new fields or explains and coördinates previously unrelated facts. The scientist needs imagination in creating new hypotheses no less than he needs ingenuity and skill in devising experiments to test them.

One of the greatest helps in the discovery of hypotheses and in the practical application of theoretical chemistry is mathematics. In recent years there has been a decided trend toward more extensive use of mathematics in chemistry, and the chemist has seen several of his own problems solved by physicists and mathematicians who have been led to successful hypotheses through their ability to express the experimental facts in precise mathematical terms.

Atoms and Molecules. Theoretical chemistry is concerned with matter, electricity, and radiation, and considerable progress has been made by visualizing the corresponding units — the atom, the electron, and the quantum.

A theory of atoms was known from the times of the Greek philosophers but it could not be developed until quantitative experimental facts became available. Late in the seventeenth century Boyle seems to have looked upon chemical combination as the result of atomic association. Guided by these early speculations and influenced by the writings of Sir Isaac Newton, Dalton formed a mental picture of the part played by atoms in the act of chemical combination. According

to his atomic theory, matter is composed of extremely minute, indivisible particles or atoms. Atoms of the same element are all of equal weight, but atoms of different elements have weights proportional to their combining ratios. Chemical compounds are formed by the union of atoms of different kinds, and in this way a simple, rational explanation is offered for the empirical laws of chemical combination which are known to every student of elementary chemistry.

It remained for the Italian physicist, Avogadro, in 1811 to point out the distinction between atoms and molecules. He defined the atom as the smallest particle which can enter into chemical combination, whereas the molecule is the smallest portion of matter which can exist in a free state. He then formulated the following hypothesis:

"Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules." This hypothesis has been important in the development of chemistry.

Atomic Weights. Before the relation between atomic weights and molecular weights could be fully appreciated it was necessary to collect a large amount of experimental data on combining weights of elements in different compounds and to discover certain guiding principles. Dulong and Petit in 1819 pointed out that the product of the specific heat and the atomic weight is approximately 6.4 in the case of most elements and that the atomic weight of an element can be estimated by dividing this constant by the specific heat of the element. Mitscherlich in 1820 showed that in crystals which are isomorphous a similar arrangement of atoms exists and that it is possible to calculate the weight of one of these atoms if the atomic weights of all the other elements in the two isomorphous crystals are known. The problem of atomic and molecular weights was finally cleared up by Cannizzaro in 1858.

The powerful stimulus of hypotheses in furthering careful experimental work is well illustrated in this field. Shortly after the announcement of Dalton's atomic theory Berzelius set out to obtain the first table of atomic weights. A little later in 1815 Prout suggested that the atomic weights of the elements are exact multiples of the atomic weight of hydrogen. To test the accuracy of this hypothesis, Stas undertook the redetermination of the atomic weights of several elements with a high degree of accuracy. This important series of investigations disproved Prout's hypothesis as originally stated. A century later, however, we know that Prout's hypothesis is essentially correct and that the deviations from whole numbers are due largely to the existence of isotopes which have identical chemical properties but different atomic weights, each atomic weight being a whole number.

INTERNATIONAL ATOMIC WEIGHTS

1931

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.76	Neodymium	Nd	60	144 27
Argon	A	18	39 944	Neon	Ne	10	20.183
Arsenic	As	33	74.93	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9 02	Osmium	Os	76	190.8
Bismuth	Bi	83	209 00	Oxygen	O	8	16 0000
Boron	B	5	10 82	Palladium	Pd	46	106 7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195 23
Calcium	Ca	20	40 08	Potassium	K	19	39.10
Carbon	C	6	12.00	Praseodymium	Pr	59	140 92
Cerium	Ce	58	140 13	Radium	Ra	88	225 97
Cesium	Cs	55	132 81	Radon	Rn	86	222
Chlorine	Cl	17	35.457	Rhenium	Re	75	186 31
Chromium	Cr	24	52 01	Rhodium	Rh	45	102.91
Cobalt	Co	27	58 94	Rubidium	Rb	37	85 44
Columbium	Cb	41	93.3	Ruthenium	Ru	44	101.7
Copper	Cu	29	63 57	Samarium	Sm	62	150.43
Dysprosium	Dy	66	162.46	Scandium	Sc	21	45 10
Erbium	Er	68	167.64	Selenium	Se	34	79.2
Europium	Eu	63	152 0	Silicon	Si	14	28 06
Fluorine	F	9	19.00	Silver	Ag	47	107 880
Gadolinium	Gd	64	157.3	Sodium	Na	11	22 997
Gallium	Ga	31	69 72	Strontium	Sr	38	87 63
Germanium	Ge	32	72 60	Sulphur	S	16	32 06
Gold	Au	79	197 2	Tantalum	Ta	73	181.4
Hafnium	Hf	72	178 6	Tellurium	Te	52	127.5
Helium	He	2	4.002	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204 39
Hydrogen	H	1	1.0078	Thorium	Th	90	232.12
Indium	In	49	114 8	Thulium	Tm	69	169.4
Iodine	I	53	126 932	Tin	Sn	50	118.70
Iridium	Ir	77	193 1	Titanium	Ti	22	47.90
Iron	Fe	26	55 84	Tungsten	W	74	184.0
Krypton	Kr	36	82 9	Uranium	U	92	238.14
Lanthanum	La	57	138 90	Vanadium	V	23	50.95
Lead	Pb	82	207.22	Xenon	Xe	54	130.2
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.5
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.92
Magnesium	Mg	12	24 32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

Again the periodic table of Mendeleeff in 1869 led to renewed experimental activity. When the elements were arranged in the order of their atomic weights, several of them fell into groups with which their chemical and physical properties did not correspond, and Mendeleeff asserted that in these cases the commonly accepted atomic weights were erroneous. A careful redetermination of atomic weights followed and in most cases his predictions were confirmed. Finally the developments in the theory of atomic structure led Richards in 1913 to make a careful study of the atomic weight of elements from radioactive minerals; it was found that lead from different radioactive minerals has different atomic weights, thus fully establishing the theory of isotopes.

During the last thirty years the degree of precision attainable in the determination of atomic weights has been greatly increased, and the determinations carried out by T. W. Richards and his associates are universally regarded as masterpieces of experimental work. The accompanying table gives the atomic weights of the elements as published by the Committee on Atomic Weights of the International Union of Chemistry for 1931*, together with the atomic numbers, which are defined in Chap. XXI.

The Avogadro Number. Until recently, it was supposed that atomic weights could be only relative numbers, but now it is easy to calculate the actual weight in grams of an atom. The number of molecules in a gram-molecule, 6.06×10^{23}, has been called the Avogadro number, and it is a fundamental constant in physical chemistry.

The value of this constant has been determined in many different ways which are entirely independent of each other, and the agreement is remarkably close. Perrin determined the constant from observations of Brownian motion, Rutherford from a determination of the charge on the alpha particle from radium, Boltwood and Curie by direct counting of alpha particles and a measurement of the volume of helium resulting from alpha particles, and Planck from an experimental determination of the constants of radiation. The most accurate value, 6.06×10^{23}, was determined by Millikan in his classical oil-drop experiment from which he obtained the charge on the electron. The error probably does not exceed 0.1 per cent.

The weight of a single atom or molecule is obtained by dividing the respective atomic or molecular weight by the Avogadro number. For example, the weight of an atom of hydrogen is $1.008/6.06 \times 10^{23} = 1.66 \times 10^{-24}$ gram, and the weight of a molecule of hydrochloric acid is $36.46/6.06 \times 10^{23} = 6.01 \times 10^{-23}$ gram.

* J. Am. Chem. Soc., **53**, 1627 (1931).

The Avogadro number is a very large number which can hardly be visualized. Very few operations or analytical tests in chemistry can be carried out with less than a millionth of a gram-molecule, and a millionth of a gram-molecule still contains six hundred thousand million million molecules.

Electrons and Protons. Until the present century it was thought that atoms were ultimate units of elements which could not be resolved into smaller particles. It is now well established, however, that atoms are composed of dense nuclei of positive electricity surrounded by negative electricity. The units of positive electricity, hydrogen nuclei, are called protons, and the units of negative electricity are called electrons.

Electrons have a charge of 1.59×10^{-19} coulomb, and when an electrical field is applied they can travel along a metal wire. Across an evacuated tube they move with velocities depending on the applied voltage. When electrons move they generate a magnetic field and can turn the armature of an electric motor. When they pass through a wire of high resistance they generate heat; if the wire is heated to a high temperature, part of the energy is given out in the form of radiation as in the ordinary electric-light bulb. When electrons are removed from atoms, positive ions are produced, and when extra electrons are attached to atoms negative ions are produced.

During electrolysis electrons are supplied at the cathode and removed at the anode, and in general, chemical reduction corresponds to the addition of electrons and oxidation to the removal of electrons. The transfer of protons is probably responsible for the behavior of acids and bases.

Quanta. Electrons may be displaced in atoms by the absorption of energy, and light is emitted when they return to their normal positions. The electrons may be displaced by collisions with other atoms at high temperatures or with electrons or ions in an electrical field. They may be displaced also by the absorption of light. Just as matter consists of an aggregate of atoms, and electricity is composed of electrons, so light, or any form of radiant energy, consists of small units of energy called quanta. The energy, ϵ, in one of these quanta varies with the frequency, ν, in a manner given by the fundamental equation

$$\epsilon = h\nu$$

where h is the universal Planck's constant, having a value of 6.55×10^{-27} erg-second. This equation is useful in the study of spectroscopy and photochemistry and in a number of physical and chemical phenomena. It is the basis of the quantum theory, which has so

revolutionized physics and is now leading to new advances in chemistry.

Survey of Physical Chemistry. It will be helpful for the student starting the study of physical chemistry to glance over the field as indicated by the table of contents. The physical properties of gases, liquids, and crystals are described using mathematical relations whenever possible. We know most about gases, and marked advances have been made in our knowledge of crystals through X-ray analysis, but our knowledge of the nature of liquids is still very meagre. The relations between physical properties and molecular constitution are confined largely to the field of organic chemistry where the relations are comparatively simple.

The first and second laws of thermodynamics and the classical applications in physics are necessary in connection with material which follows later.

The study of solutions is concerned with various types and with quantitative vapor-pressure relations, and solubility. The vapor-pressure lowering, elevation of the boiling-point, depression of the freezing-point, and osmotic pressures are easily calculated for ideal solutions, but the situation is more complicated when electrically charged ions or concentrated solutions are involved.

Colloids with their very large surfaces bring into play new factors such as electrical charges and hydration, thereby introducing many new phenomena which are of practical importance.

Thermochemistry is concerned with the relations between heat and chemical reactions. The expression of a chemical equilibrium constant answers the question "How far will the reaction go?" The calculation of these equilibrium constants and the influence of temperature and pressure are of great value. For the sake of convenience this subject is divided into homogeneous equilibria, in which the physical and chemical properties are uniform throughout, and heterogeneous equilibria, in which surfaces of solids or liquids are involved. In the latter case the Phase Rule of Willard Gibbs plays an important part.

The question of the speed of a chemical reaction is considered in kinetics. Mathematical expressions of reaction rate and mechanisms of reaction and catalysis are parts of this field.

The relations between chemical reaction and electricity may be divided into phenomena dealing with electrical current, phenomena dealing with voltage, phenomena dealing with electrolysis, and phenomena dealing with equilibria between ions in solution.

After the study of chemical equilibria and electrochemistry, it is

profitable to apply the science of thermodynamics to chemical reactions and to show how the extent to which a reaction will go can be predicted from a knowledge of free energies and entropies.

Photochemistry is concerned with the influence of light on chemical reactions.

Our understanding of the structure of the atom has increased greatly in recent years, and this knowledge is leading to new progress in several branches of physics and chemistry. The experimental foundations of these theories are laid in the electrical properties of matter and in the phenomena of radioactivity.

CHAPTER II

GASES

The Gas Laws. Matter in the gaseous state possesses the property of filling completely and to a uniform density any available space. Among the most pronounced characteristics of gases are lack of definite shape or volume, low density and small viscosity. The laws expressing the behavior of gases under different conditions are relatively simple and to a large extent are independent of the nature of the gas. The temperature and pressure coefficients of expansion of all gases are very nearly the same.

In 1662, Robert Boyle discovered the familiar law that *at constant temperature, the volume of a gas is inversely proportional to the pressure.* This may be expressed mathematically as follows: —

$$v \propto \frac{1}{p} \text{ (temperature constant)}, \tag{1}$$

where v is the volume and p the pressure.

In 1801, Gay-Lussac discovered the law of the variation of the volume of a gas with temperature: — *At constant pressure, the volume of a gas is directly proportional to its absolute temperature,** or

$$v \propto T \text{ (pressure constant)}. \tag{2}$$

There are three conditions which may be varied, viz., volume, temperature and pressure. The preceding laws have dealt with the relation between two pairs of the variables when the third is held constant. There remains to consider the relation between the third pair of variables, pressure and temperature, the volume being kept constant. Evidently a necessary corollary of the first two laws is, that *at constant volume, the pressure of a gas is directly proportional to its absolute temperature,* or

$$p \propto T \text{ (volume constant)}. \tag{3}$$

The expressions (1) and (2) may be combined to give (4)

$$v \propto \frac{T}{p} \tag{4}$$

* The symbol T is used for absolute temperature.

and introducing a proportionality factor

$$v = k\frac{T}{p}$$

or

$$pv = kT. \tag{5}$$

If the equation is applied to one mol of gas (i.e., the molecular weight of the gas taken in grams), the molar gas constant, R, may be used in place of the constant k. The equation is made more general by introducing the factor n, which represents the number of gram-molecules taken.

The common expression for the simple gas laws then is

$$pv = nRT \tag{6}$$

and when $n = 1$, $pv = RT$.

Evaluation of the Molar Gas Constant. It will be remembered that a force multiplied by distance represents work, and since the product pv represents work, R must be expressed in energy units divided by temperature. The numerical value of R may be obtained from experimental measurements, usually at a pressure of one atmosphere and a temperature of 0° C. (273.1° K.) Under these conditions, when $n = 1$, the volume, v, is 22.412 liters. Several different energy units may be employed as shown in the following calculations.

1. *R in liter-atmospheres per degree.*

$$R = \frac{pv}{T} = \frac{1 \text{ atmosphere} \times 22.412 \text{ liters}}{273.1} = 0.08206 \text{ liter-atmosphere.}$$

2. *R in cc.-atmospheres per degree.*

$$R = \frac{pv}{T} = \frac{1 \text{ atmosphere} \times 22{,}412 \text{ cc.}}{273.1} = 82.06 \text{ cc.-atmospheres.}$$

3. *R in joules per degree.*

The pressure may be changed to dynes by multiplying the barometer height, 76 cm. of mercury, by the density of mercury, 13.596, and the acceleration of gravity, 980.6 cm. per sec. per sec. The pressure in dynes per square centimeter multiplied by the volume in cubic centimeters gives the energy in ergs. Ergs in turn are converted into joules by dividing by 10^7.

$$R = \frac{pv}{T} = \frac{76.0 \times 13.596 \times 980{\cdot}6 \times 22{,}412}{273.1 \times 10^7} = 8.315 \text{ joules per degree.}$$

4. *R in calories per degree.*

Joules may be converted into calories by dividing by the mechanical equivalent of heat, 4.185.

$$R = \frac{8.315}{4.185} = 1.987 \text{ cal. per degree.}$$

In calculations involving the gas laws it is usually most convenient to express R in liter-atmospheres or in cc.-atmospheres; in electrochemical problems involving volts and coulombs, R is best expressed in joules; and in thermo-chemical and thermodynamical problems R is usually given in calories. It is necessary to be thoroughly familiar with the different constants and to know which units to use in a specified problem and how to convert one into another.

Deviations from the Gas Laws. Careful experiments by Amagat* and others on the behavior of gases over extended ranges of

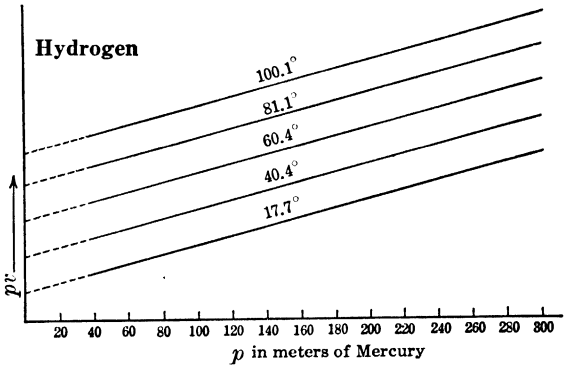


FIG. 1

temperature and pressure have shown that the fundamental gas equation, $pv = nRT$, is not strictly applicable, the deviations depending upon the nature of the gas and the conditions under which it is observed. It has been shown that the gas laws are more nearly obeyed the lower the pressure, the higher the temperature, and the further the gas is removed from the critical state. A gas which would conform to the requirements of the fundamental gas equation is called an *ideal* or *perfect gas*. Almost all gases are far from ideal in their behavior, and the underlying causes are the same in all gases. At constant temperature the product, pv, in the gas equation is constant, so that if we plot pressures as abscissas and the corresponding values of pv as ordinates, for an ideal gas we should obtain a straight line

* Ann. chim. phys., (5), **19**, 345 (1880).

parallel to the axis of abscissas. The results obtained with five typical gases are shown in the accompanying diagrams, Figs. 1 to 3. It is apparent that all these gases depart widely from ideal behavior. In

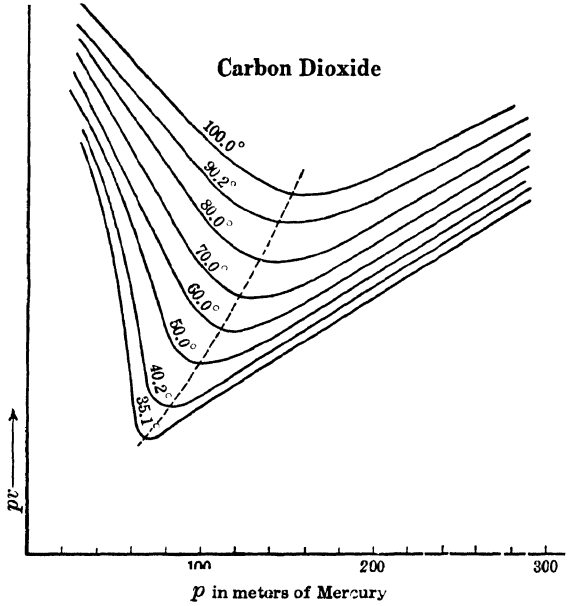


FIG. 2

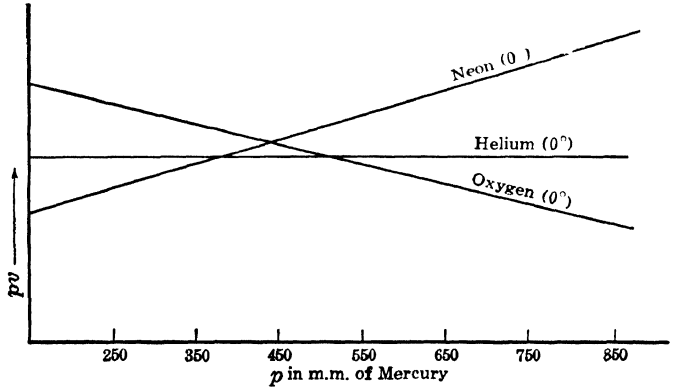


FIG. 3

the case of hydrogen and neon pv increases continuously with the pressure, whereas with carbon dioxide it first decreases, attains a minimum value, and then increases with increasing pressure. Oxygen gives a straight line with a negative slope, while helium gives a perfectly horizontal line.

All gases are alike in showing, under the proper conditions, a minimum in the curve like that of carbon dioxide. Some temperatures can be found at which they are more compressible than a perfect gas under low pressures, and less compressible under high pressures. The examples shown in Figs. 1 and 3 do not happen to correspond to the right temperature and pressure range to exhibit this minimum. Even helium fails to give a horizontal line at high pressures.

The deviation from the simple gas law $pv = nRT$ can be understood better after a consideration of van der Waals' equation.

Equation of van der Waals. Natterer was the first to show that the product of pressure and volume for hydrogen at room temperature is higher than it should be. A possible explanation of this departure from the gas laws was offered by Budde, who proposed that the volume, v, in the equation $pv = nRT$, should be corrected for the volume occupied by the molecules themselves. If this volume correction is denoted by b, then the gas equation becomes

$$p(v - b) = nRT, \tag{7}$$

where b is a constant for each gas. Budde calculated the value of b for hydrogen and found it to remain constant for pressures varying from 1000 to 2800 meters of mercury.

While Budde's modification of the gas equation is quite satisfactory in the case of hydrogen, it fails when applied to other gases. In general, the compressibility at low pressures is considerably greater than can be accounted for by Boyle's law. The compressibility reaches a minimum value, and then increases rapidly, so that pv passes through the value required by the law. This suggests that there is some other correction to be applied in addition to the volume correction introduced into the gas equation by Budde. In 1879, van der Waals pointed out that Boyle's law can be derived on the assumption that the molecules exert no mutual attraction, and that this assumption is undoubtedly justifiable when the molecules are far apart at low pressures; it no longer remains so when the gas is strongly compressed. A little consideration will make it apparent that when increased pressure is applied to a gas, the resulting volume will become less than that calculated, owing to molecular attraction. In other words the molecular attraction and the applied pressure act in the same direction and the gas behaves as if it were subjected to a pressure greater than that actually applied. It was shown by van der Waals that this correction is inversely proportional to the square of the volume, and since it augments the applied pressure, the expression, $p + a/v^2$,

should be substituted for p in the gas equation, a being the constant of molecular attraction. The corrected equation then becomes

$$(p + a/v^2)(v - b) = RT. \tag{8}$$

This is known as the equation of van der Waals. It is applicable not only to strongly compressed gases, but to liquids as well. Though it will be given detailed consideration in a subsequent chapter, it may be of interest to point out at this time the satisfactory explanation which it offers of the experimental results of Amagat (p. 11). When v is large, both b and a/v^2 become negligible, and van der Waals' equation reduces to the simple gas equation, $pv = nRT$. We may predict, therefore, that any influence tending to increase v will cause the gas to approach more nearly to the ideal condition. This is in accord with the results of Amagat's experiments, which show that an increase in temperature at constant pressure, or a diminution of pressure at constant temperature, causes the gas to tend to follow the simple gas laws. The equation also offers a satisfactory explanation of the exceptional behavior of hydrogen when it is subjected to pressure. As we have seen, pv for all gases diminishes at first with increasing pressure, reaches a minimum value, and then increases regularly. Since the volume correction in van der Waals' equation acts in opposition to the attraction correction, it is apparent that at low pressures the effect of attraction preponderates, whereas at high pressures the volume correction is relatively of more importance. At some intermediate pressure the two corrections counterbalance each other, and it is at this point that the gas follows Boyle's law strictly. The exceptional behavior of hydrogen may be accounted for by making the very plausible assumption that the attraction correction is negligible at all pressures in comparison with the volume correction.

This attractive force between molecules, designated by a in van der Waals' equation, is responsible for the condensation of gases to liquids. It is natural that those gases which are far above their boiling-points, like hydrogen and helium at room temperature, should have very small attractive forces and should not exhibit the phenomenon of abnormally large compressibility. Furthermore, at high pressures all gases show abnormally small compressibility because under these conditions the molecules themselves occupy an appreciable fraction of the total volume and are comparatively incompressible. A table is given on p. 36 wherein the simple gas law is compared with van der Waals' equation for various gases under different conditions.

Gas Density and Molecular Weight. Oxygen is given an atomic weight of 16 as an arbitrary standard in determining the atomic

weights of other elements. In the same way 32 is taken as the standard for molecular weights, since oxygen is diatomic, and it has been found experimentally that 32 grams of oxygen occupies a volume of 22.412 liters at 0° C. and 760 mm. pressure after correcting for the deviations from the perfect gas laws. To determine the molecular weight of a gas, then, it is only necessary to find the weight of 22.412 liters of the gas at 0° and 760 mm. pressure since by Avogadro's law equal volumes of gases contain the same number of molecules under the same conditions of temperature and pressure. *Gas density* is defined as the weight of one liter of the gas. Sometimes the density of a gas is expressed in terms of the ratio of the density to the density of some standard gas such as air or hydrogen.

It is inconvenient to weigh a volume of gas or vapor under standard conditions of temperature and pressure, but by means of the gas laws the determination, made at any temperature and under any pressure, can be reduced to standard conditions. For example, suppose v cc. of gas is found to weigh g grams at $t°$ and p mm. pressure, then the weight in grams of 22.412 liters or 22,412 cc. at 0° and 760 mm. will be given by the following proportion, in which M denotes the molecular weight of the substance: —

$$g : \frac{pv}{t + 273.1} = M : \frac{760 \times 22{,}412}{273.1},$$

or

$$M = \frac{g \times 760 \times 22{,}412 \times (t + 273.1)}{273.1\ pv}. \tag{9}$$

The determination of vapor density may be effected in either of two ways: (1) we may determine the mass of a known volume of vapor under definite conditions of temperature and pressure, or (2) we may determine the volume of a known mass under definite conditions of temperature and pressure. There are a variety of methods for the determination of vapor density; but for our purpose it will be necessary to describe but two of them. In the method of Regnault the mass of a definite volume of vapor is determined, whereas in the method due to Victor Meyer we measure the volume of a known mass.

Method of Regnault. This method makes use of two spherical glass bulbs of approximately the same capacity, each bulb being provided with a well-ground stop-cock. By means of an air pump one bulb is evacuated as completely as possible, and is then filled, at definite temperature and pressure, with the gas whose density is to be determined. The stop-cock is then closed and the bulb weighed, the

second bulb being used as a counterpoise. The use of the second bulb is largely to avoid the troublesome corrections for air displacement and for moisture, each bulb being affected in the same way and to nearly the same extent. The volume of the bulb may be obtained by weighing it first evacuated, and then filled with distilled water at known temperature. From these results we may calculate the mass per unit of volume; or we may substitute the values of w, v, p, and t in the above formula and calculate M, the molecular weight. This method was used by Morley* in his research on the densities of hydrogen and oxygen, and has been used in the most recent and accurate determinations of the same constants.

Method of Victor Meyer. The convenient method of Victor Meyer is used to determine the molecular weight of an easily condensable gas. A weighed amount g of a liquid is vaporized, and the volume of air displaced is measured at room temperature and under existing barometric pressure. This volume is the same as that which the vapor would occupy if it could be cooled to room temperature without condensation. The apparatus is shown in Fig. 4. The tube A is suspended in a heating jacket B at a temperature about 30° above the vaporizing temperature of the substance under investigation. The side tube E leads to a gas burette and leveling tube filled with water, or better, with mercury. The neck of the tube A is long and narrow (75 cm. by 1 cm.) in order to minimize diffusion and condensation of the vapor outside the jacket. A small bulb containing a known weight of the substance whose vapor density is sought is inserted in the upper part of the tube A and is prevented from falling by means of a glass rod D projecting through the side tube C. The joint between D and C is made with rubber tubing so that the glass rod may be pulled outward to release the bulb. Before the bulb is released the whole apparatus is tested to insure that the temperature is constant and that the apparatus is gas-tight. When the bulb falls to the bottom of the tube A the liquid is vaporized, and the increase in volume v, due to the vaporization, is measured in the burette. If water is used in the burette, it is necessary in determining the effective pressure p to subtract the vapor pressure of the water from the observed barometric pressure. The temperature t used in the calculation is the temperature at which the air is measured, and it is not necessary to know the temperature of the jacket as long as it remains constant.

The molecular weight is calculated from the values of g, p, v, and t, using formula (9) as illustrated in the following example: 0.1050 g.

* Smithsonian Contributions to Knowledge (1895).

of benzene was weighed out, and when vaporized 33.55 cc. of air was collected over water at 20.0° and 740.5 mm. pressure. The vapor pressure of water at 20.0° is 17.5 mm., and the actual pressure exerted by the air is 740.5 − 17.5 = 723.0. Then

$$M = \frac{0.1050 \times 760 \times 22{,}412 \times (20.0 + 273.1)}{273.1 \times 723.0 \times 33.55} = 79.1.$$

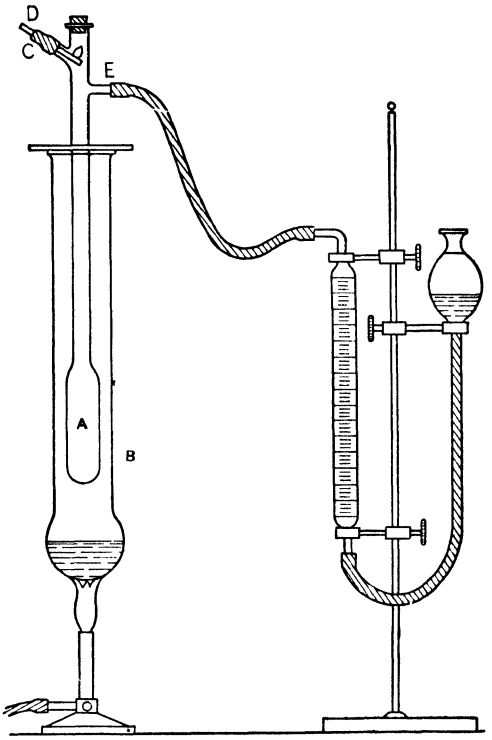


FIG. 4

The result agrees fairly well with the molecular weight of benzene (78.05) calculated from the sum of the atomic weights. The results cannot agree exactly, because the vapors, a few degrees above their boiling-points, do not behave as perfect gases and the force of attraction between the molecules brings more molecules into a given volume and leads to higher molecular weights. Further, the correction for the vapor pressure of water is not entirely satisfactory.

An approximate value of the molecular weight obtained in this way is sufficiently accurate to enable one to choose between the simple formula weight, given by chemical analysis, and some multiple of it.

The Lumsden method* is an improvement over the Victor Meyer method in which the volume is kept constant and the pressure is measured. The uncertain correction for the vapor pressure of water is eliminated. The increase in pressure produced by the vaporization of a weighed amount of liquid is measured on a mercury manometer connected through a tube of small bore with the calibrated chamber of about 100-cc. capacity.

Results of Vapor-Density Determinations. As the result of numerous vapor-density determinations extending over a wide range of temperatures, much important information has been collected concerning the number of atoms contained in the molecules of a large number of chemical compounds. The molecular weights of non-metallic, elementary gases are double their atomic weights, showing that their molecules are diatomic. In like manner the molecular weights of mercury, zinc, cadmium and, in fact, all of the vaporizable metallic elements have been found to be identical with their atomic weights. The molecules of sulphur, arsenic, phosphorus and iodine are polyatomic, if they are not heated to too high a temperature. The investigations of Meyer and others have shown that the densities of many substances diminish abnormally at higher temperatures. In other words, as the temperature is raised the number of atoms contained in the molecules decreases. The molecular weight of sulphur, calculated from its vapor density at temperatures below 500°, corresponds to the formula S_8. If the vapor of sulphur is heated to 1100°, the molecular weight corresponds to the formula S_2. In fact, sulphur in the form of vapor may be represented by the formulas S_8, S_4, S_2, or even S according to the temperature at which its vapor density is determined. Iodine behaves similarly, the molecules being diatomic between 200° and 600°, while at temperatures above 1400° the vapor density has about one-half its value at the lower temperature, showing a complete breaking down of the diatomic molecules into single atoms. Heating to yet higher temperatures has failed to reveal any further decomposition. This phenomenon is not confined to the molecules of the elements alone, but is also met with in the case of the molecules of chemical compounds. The vapor density of arsenious oxide between 500° and 700° corresponds to the formula As_4O_6. As the temperature is raised, the vapor density becomes steadily smaller until, at 1800°, the calculated molecular weight corresponds to the formula As_2O_3. In like manner ferric and aluminum chlorides have been shown to have molecular weights at low temperatures corresponding to the formulas, Fe_2Cl_6 and Al_2Cl_6. The

* J. Chem. Soc., **83**, 342 (1903).

experimental difficulties attending vapor-density determinations increase as the temperature is raised, owing chiefly to the deformation of the apparatus when the material of which it is constructed approaches its melting-point. Glass, which can be used at relatively low temperatures only, has been replaced by specially resistant varieties of porcelain which may be used up to temperatures of 1500° or 1600°. Platinum vessels retain their shape up to temperatures between 1600° and 1700°. Measurements up to 2000° have been effected by Nernst and his collaborators.* In their experiments use was made of a vessel of iridium, the inside and outside of which was surrounded with a cement of magnesia and magnesium chloride, the entire apparatus being heated electrically. With this apparatus they showed that the molecular weight of sulphur between 1800° and 2000° is 48, indicating that the diatomic molecule is approximately 50 per cent broken down into single atoms.

Abnormal Vapor Densities. In all the cases cited above the molecular weight calculated from the vapor density corresponds either with the simple formula weight, as determined by chemical analysis, or with a larger weight. In no case is there any evidence of a breaking down of the simple molecule into its constituents. Substances are known, however, the molecular weights of which, calculated from their vapor densities, are less than the sum of the atomic weights of their constituents. For example, the molecular weight of ammonium chloride at 350° was found to be 29.04, while that corresponding to the formula NH_4Cl should be 53.5. Similar results have been obtained with phosphorus pentachloride, nitrogen tetroxide, chloral hydrate and numerous other substances. The phenomenon can be explained in either of the two following ways: (1) that the molecule has undergone a complete disruption, or (2) that the substance does not follow the law of Avogadro. Until the former explanation was shown to be correct, the latter was accepted and for a time the law of Avogadro fell into disrepute. In 1857, Deville showed that numerous chemical compounds are broken down or " dissociated " at high temperatures. Shortly afterward Kopp suggested that the abnormal vapor densities of such substances as ammonium chloride and phosphorus pentachloride might be due to thermal dissociation. If ammonium chloride underwent complete dissociation, one molecule of the salt would yield one molecule of ammonia and one molecule of hydrochloric acid gas, and the vapor density of the resulting mixture would be one-half of that of the undissociated substance, a deduction in complete agreement with the results of experiment. It

* Wartenberg., Z. anorg. Chem., **56**, 320 (1907).

remained to prove that the products of this supposed dissociation were actually present.

The presence of ammonia and hydrochloric acid in the heated vapor of ammonium chloride was proved by Than* with the experiment shown in Fig. 5. The ammonium chloride was placed at F in the horizontal tube AB, and a porous plug of compressed ammonium chloride was introduced at G. The tube was heated while nitrogen

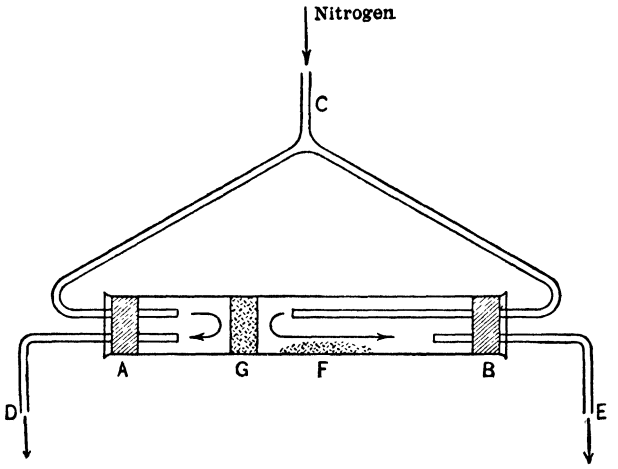


FIG. 5

was introduced at C. The exit gases were tested with litmus paper and it was found that the gas escaping from D was alkaline while that issuing from E was acid. The ammonium chloride is dissociated at the high temperature into ammonia and hydrochloric acid and the ammonia, being lighter, diffuses faster through the plug G and passes out through D. Experiments on other substances whose vapor densities are abnormally small show that a similar explanation is applicable and furnish further confirmation of Avogadro's law.

Calculation of the Degree of Dissociation. The density of a dissociating vapor decreases with increase in temperature, and it is important to know the degree of dissociation at any one temperature. The degree of dissociation is a measure of the extent to which the dissociating reaction has proceeded, and for example in the reaction

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

it measures the extent to which the reaction has proceeded from left to right. It can be determined easily by measuring the vapor density.

* Lieb. Ann., **131**, 129 (1864).

If we start with one mol* of gas and let α represent the fraction dissociated, then $1 - \alpha$ will denote the fraction remaining undissociated. If one mol of gas yields n mols of gaseous products, the total number of mols present at any time will be

$$(1 - \alpha) + n\alpha \quad \text{or} \quad 1 + (n - 1)\,\alpha.$$

Since the density of a given weight of gas is *inversely* proportional to the number of mols, the ratio of the density, d_2, of the dissociated gas to the density, d_1, of the undissociated gas is given by the following expression:

$$\frac{d_2}{d_1} = \frac{1}{1 + (n - 1)\,\alpha}, \tag{10}$$

and

$$\alpha = \frac{d_1 - d_2}{d_2\,(n - 1)}. \tag{11}$$

Molecular weights may be substituted for densities, giving

$$\alpha = \frac{m_1 - m_2}{m_2\,(n - 1)}, \tag{12}$$

where m_1 is the molecular weight of the undissociated gas and m_2 is the average molecular weight of the gases after dissociation. Molecular weights are obtained by multiplying the densities by the gram-molecular volume — i.e., by $\left(22.4 \times \frac{T}{273} \times \frac{760}{p}\right)$, or by $\frac{RT}{p}$.

Sometimes the densities are given in terms of the ratio of the density of the gas to the density of a standard gas of known molecular

THE DISSOCIATION AND DENSITIES OF NITROGEN TETROXIDE (N_2O_4) AT ONE ATMOSPHERE PRESSURE

Temp. (°C.)	Mean Molecular Weight Dissociated gas (m_2)	$\alpha = \frac{92 - m_2}{m_2}$
15	82 00	0.1216
25	77.64	0.1845
35	72 45	0.2700
45	66.80	x
55	61.24	0.5021
65	56.51	0.6283
75	52.85	0.7408

* One mol is a quantity in grams equal to the molecular weight.

weight such as hydrogen or oxygen or air. It will be noted that the value of α is not affected by using different standards of density because any constant factor appears in both the numerator and denominator and cancels out.

The application of this formula to nitrogen tetroxide is illustrated in the table. In this case two molecules of NO_2 are produced by the dissociation of one molecule of N_2O_4 and $(n - 1)$ has the value **1.** The mean molecular weight, m_2, of the dissociated gas is determined experimentally and m_1 is taken as the theoretical molecular weight of undissociated nitrogen tetroxide (N_2O_4), i.e., 92.

Kinetic Theory of Gases. The first attempt to explain the properties of gases on a purely mechanical basis was made by Bernoulli in 1738. Subsequently, through the labors of Kroenig, Clausius, Maxwell, Boltzmann, and others, his ideas were developed and assumed mathematical form as the kinetic theory of gases.

The essential feature of the kinetic theory is that heat energy in matter is a manifestation of the motion of the ultimate particles of which the matter is composed. In a liquid or solid these particles — molecules, atoms, or ions — vibrate about their positions of equilibrium; as the temperature increases, the vibrations become more and more vigorous, until finally the heat motions cause the particles to break away from the restraining forces holding them together, and the substance vaporizes. The molecules of the gas thus formed no longer vibrate in the neighborhood of one point, but are completely separated from one another and move in straight lines with a velocity determined by the temperature of the gas. The volume occupied by the molecules themselves is much smaller than the volume filled by them, so that a molecule can move for a considerable distance before it collides with one of its neighbors; the distance through which such a molecule moves between collisions is called its *mean free path.* The combined effect of the impacts of the moving molecules upon the walls of the containing vessel accounts for the pressure exerted by the gas. When a gas expands, it does work at the expense of the kinetic energy of its molecules, and we say that it loses heat.

Derivation of the Kinetic Equation. Starting with certain assumptions, it is possible to derive in a simple fashion an equation from which the gas laws may be deduced. Imagine n molecules, each having a mass m, confined within the cubical vessel shown in Fig. 6, the edge of which has a length l cm. Let us assume that the molecules are negligibly small compared with the distances between them, that there are no forces between the molecules and that the collisions of the molecules with each other and with the sides of the box are

perfectly elastic. Though the different molecules are doubtless moving with different velocities, there must be an average velocity for all of them; let this be denoted by u. As a result of their collisions with each other inside the box, the molecules will be moving sometimes in one direction, sometimes in another; since these directions may be resolved along three different axes at right angles to each other, it may be supposed that one-third of the molecules are moving always in the direction perpendicular to the wall A. Let us consider the collisions of the molecules with A. Any molecule will strike A every $2l$ cm. as it moves back and forth across the box. If its velocity is u, it will collide with A, $\frac{u}{2l}$ times per second. Since the collisions are perfectly elastic, the molecule will rebound with velocity $-u$, having suffered no loss in kinetic energy. The momentum before collision was mu and after collision is $-mu$, so that the change in momentum per collision per molecule is $2mu$. There are $\frac{u}{2l}$ collisions per second, so the change in momentum per molecule per second is $\frac{mu^2}{l}$. The total change in momentum per second for the $\frac{n}{3}$ molecules which can collide with A is $\frac{n}{3}\frac{mu^2}{l}$; this represents the average force on A, since the time rate of change in momentum gives force. If we remember that pressure is force per unit area, the pressure on A is seen to be

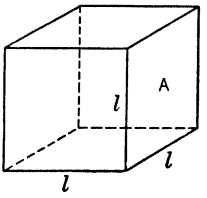


FIG. 6

$$p = \frac{\text{Force}}{\text{Area}} = \frac{1}{l^2}\frac{n}{3}\frac{mu^2}{l}. \tag{13}$$

But l^3 is precisely the volume of the box, and we have

$$p = \frac{n}{3}\frac{mu^2}{v} \tag{14}$$

or

$$pv = \tfrac{1}{3}nmu^2 \tag{15}$$

This is the fundamental equation of the kinetic theory of gases. Though the equation has been derived for a cubical vessel, it is equally applicable to a vessel of any shape whatever, since the total volume may be considered to be made up of a large number of infinitesimally small cubes, for each of which the equation holds.

Deductions from the Kinetic Equation. The kinetic equation may be written in the form

$$pv = \tfrac{2}{3} \cdot \tfrac{1}{2}nmu^2. \tag{16}$$

Since the kinetic energy of a moving body is given by the expression $\frac{1}{2} mu^2$, the total kinetic energy of the molecules of the gas is $\frac{1}{2} nmu^2$. Therefore *the product of the pressure and volume of the gas is equal to two-thirds the total kinetic energy of its molecules.*

If the temperature of the gas remains constant, the kinetic energy of the gas remains constant, since, according to the kinetic theory, the heat energy of a system is nothing else than the kinetic energy of the system. The product pv must then be constant at constant temperature; this is clearly Boyle's law. Since the mean kinetic energies of all gases are identical at the same temperature, it follows that any change in the kinetic energy resulting from a change in temperature must be directly proportional to the latter, otherwise the mean kinetic energies of the gas molecules which were equal at one temperature could not be so at any other. But equation (16) shows that the product of the pressure and volume of a gas is directly proportional to the total kinetic energy of its molecules, and a change in temperature must therefore alter this product to the same extent for each gas. If the pressure is maintained constant, the volume alone will undergo change, or vice versa, if the volume remains constant the pressure only will be altered. In either case, whichever factor of the product, pv, undergoes change, the kinetic theory shows that the rate of this change with temperature is the same for all gases. This, it will be observed, is a statement of the law of Gay-Lussac.

As noted in the preceding paragraph, a change in temperature changes the kinetic energy to the same extent for each gas; hence the kinetic energy must be proportional to the temperature. It remains only to choose the proportionality constant. If temperature is measured on the absolute scale, and N is the number of molecules in one mol of gas, this proportionality constant is R, the molar gas constant, and we have

$$pv = \tfrac{2}{3} \cdot \tfrac{1}{2} Nmu^2 = RT, \tag{17}$$

the equation of state for a perfect gas.

If equal volumes of two different gases are measured under the same pressure, we have

$$pv = \tfrac{1}{3} n_1 m_1 u_1^2 = \tfrac{1}{3} n_2 m_2 u_2^2, \tag{18}$$

where n_1 and n_2, m_1 and m_2, and u_1 and u_2 denote the number, mass and velocity of the molecules in the two gases. If the gases are measured at the same temperature, the molecules of each possess the same mean kinetic energy, or

$$\tfrac{1}{2} m_1 u_1^2 = \tfrac{1}{2} m_2 u_2^2. \tag{19}$$

Dividing equation (18) by equation (19), we have

$$n_1 = n_2,$$

or under the same conditions of temperature and pressure equal volumes of the two gases contain the same number of molecules. This is the hypothesis of Avogadro.

Effusion of Gases. If the fundamental kinetic equation is solved for u, we have

$$u = \sqrt{\frac{3\,pv}{mn}}; \tag{20}$$

but $v/mn = 1/d$, where d is the density of the gas, and therefore we may write

$$u = \sqrt{\frac{3\,p}{d}}. \tag{21}$$

If the pressure and temperature remain constant, it is evident that the mean velocities of the molecules of two gases are inversely proportional to the square roots of their densities, a law which was first enunciated by Graham as the result of his experiments on gaseous effusion.

Graham's law receives practical application in the rate of effusion of gases and in the determination of molecular weights. If u_1 and u_2 denote the mean velocities of two different gases which have densities d_1 and d_2, and molecular weights M_1 and M_2, then according to equation (21) at constant temperature and pressure,

$$\frac{u_1}{u_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}. \tag{22}$$

When two different gases are forced through a *small* aperture, the times t_1 and t_2 taken for each gas to pass through under a given pressure difference are *inversely* proportional to the velocities of the gas molecules. Combining this relation with that of equation (22) it follows that

$$\frac{t_1}{t_2} = \frac{u_2}{u_1} = \sqrt{\frac{M_1}{M_2}}. \tag{23}$$

Bunsen developed this method for determining the molecular weight of a gas by comparing its time of effusion with that of a gas of known molecular weight. It has proved to be a convenient method and one which is particularly valuable in cases where only a small amount of material is available. For example, Debierne* determined the molecu-

* Debierne, Compt. rend., **150**, 1740 (1910).

lar weight of radon (radium emanation) with an accuracy of two per cent using only 1 cu. mm. of the gas.

Mean Velocity of Translation of a Gaseous Molecule. By substituting appropriate values for the various magnitudes in the equation

$$u = \sqrt{\frac{3\,pv}{mn}},$$

it is possible to calculate the mean velocity of the molecules of any gas. Thus, for the gram-molecule of hydrogen at 0° and 76 cm. pressure, $p = 76 \times 13.596 = 1033.3$ gr. per sq. cm. $= 1033.3 \times 980.6$ dynes per sq. cm., $v = 22{,}412$ cc., and $mn = 2.016$ gr.

Substituting these values in the above equation we have,

$$u = \sqrt{\frac{3 \times 1033.3 \times 980.6 \times 22{,}412}{2.016}} = 183{,}780 \text{ cm. per sec.}$$

Thus at 0° the molecule of hydrogen moves with an average speed greater than one mile per second.

Specific Heat of Gases. In the preceding discussion of the kinetic theory of gases it was assumed that the molecules are simple units incapable of absorbing any energy except that used in changing their velocities. This assumption is justified only in a few cases and further insight into the behavior of gases may be obtained through a study of specific heats. The heat capacity c of a substance is the ratio of the amount of heat supplied, to the temperature rise; and the specific heat is the heat capacity per gram.

If a gas is heated at constant pressure, more heat will be required to raise it one degree than if it is heated at constant volume because in the former case the gas will expand and do work against the atmosphere. The recognition by Mayer, in 1841, of the cause of this difference between the two specific heats of a gas, led him to his celebrated calculation of the mechanical equivalent of heat and the enunciation of the first law of thermodynamics.

The specific heat at constant pressure is denoted by c_p, the specific heat at constant volume is denoted by c_v, and these specific heats are multiplied by the molecular weight to give the molar heat capacities C_p and C_v.

The difference between the two specific heats may be easily calculated from the gas law

$$pv_1 = RT_1,$$

where v_1 is the volume of 1 mol of gas at temperature T_1 and R is the molar gas constant. When the gas is heated at constant pressure to

temperature T_2, the volume increases to v_2 and the work done is the product of the pressure and the increase in volume, or

$$p(v_2 - v_1) = R(T_2 - T_1). \tag{24}$$

If $T_2 - T_1 = 1°$, then the equation reduces to

$$p(v_2 - v_1) = R.$$

Since the difference between the molar heat at constant pressure and constant volume is equivalent to the external work involved when the temperature of 1 mol of gas is raised 1°, we have

$$C_p - C_v = Mc_p - Mc_v = p(v_2 - v_1) = R = 1.987 \text{ cal.} \tag{25}$$

In words the difference between the molar heat capacity at constant pressure of any gas and the heat capacity at constant volume is equal to the gas constant R, approximately 2 calories per degree.

The specific heat of a gas at constant pressure may be readily obtained by determining the number of calories necessary to raise the temperature 1° while a definite quantity of gas is streaming through the apparatus. The determination of the specific heat at constant volume is much more difficult because any containing vessel designed to maintain the volume constant absorbs a great deal more heat than does the gas itself. Measurements of this kind in which the corrections are many times greater than the quantity to be measured are inaccurate. The molar heat capacity at constant volume is obtained by indirect methods, subtracting 2 calories from the molar heat capacity at constant pressure as given in equation (25), or by direct experimental determination of the ratio c_p/c_v.

The Ratio of the Two Specific Heats. The method of Clément and Desormes for determining the ratio c_p/c_v depends on the fact that when a gas expands quickly it does not have time to absorb heat from the containing vessel. There is a simple relation between the expansion of a gas under these conditions and the ratio c_p/c_v. The gas to be investigated is introduced into a large glass vessel under a pressure which is only slightly greater than atmospheric pressure. The large vessel is provided with a sensitive manometer and a stop-cock of large bore. The stop-cock is opened to allow the pressure within the vessel to fall to that of the atmosphere, after which it is immediately closed. The expansion of the gas resulting from the momentary opening of the flask causes a slight lowering of the temperature. Thermal equilibrium is again restored by the influx of heat from without, which in turn causes the pressure to increase to a value slightly greater

than atmospheric pressure. If this excess of pressure over atmospheric pressure is designated by p_2 and the original excess of pressure over atmospheric pressure by p_1, it can be shown that

$$\frac{c_p}{c_v} = \frac{p_1}{p_1 - p_2} \tag{26}$$

This equation is only approximate and it holds more accurately when p_1 and p_2 are very small and when the time taken for expansion is very short.

When a sound wave passes through a gas, the alternate compressions and expansions of the gas are exceedingly rapid and the phenomenon is particularly well suited for the determination of the ratio c_p/c_v.

The velocity v of transmission of a sound wave in a gas is given by the formula of Laplace

$$v = \sqrt{\gamma \frac{p}{d}} \tag{27}$$

in which p and d denote the pressure and density of the gas and γ is the ratio of the two specific heats, c_p/c_v.

In the method of Kundt the velocity of sound is measured in two different gases at the same pressure and the value of γ for one gas is obtained from a knowledge of γ for a second gas, using the formula

$$\frac{v_1}{v_2} = \sqrt{\frac{\gamma_1 m_2}{\gamma_2 m_1}}. \tag{28}$$

This formula is obtained directly from Laplace's formula by dividing, by substituting the ratio of molecular weights m for the ratio of densities, and by using subscripts 1 and 2 for the first and second gases, respectively.

The velocity of sound v is determined by measuring the distance between stationary waves set up in a long glass tube containing the gas. Lycopodium powder is spread over the bottom, and when the tube is made to vibrate longitudinally, emitting a shrill note, the powder arranges itself in a series of heaps corresponding to nodes of vibration. Under these conditions the velocity of sound is proportional to the distance between nodes. Air, with a molecular weight of 28.74 and a value of γ of 1.405, is usually used for the reference gas in this method.

Specific Heat of Gases and the Kinetic Theory. When a monatomic gas, such as helium or mercury vapor, is heated at constant volume the heat energy supplied is used to augment the translational kinetic

energy of the molecules. As we have seen in equation (15), the fundamental kinetic equation

$$pv = \tfrac{1}{3}\, mnu^2$$

may be written

$$pv = \tfrac{2}{3}\,\tfrac{1}{2}\, mnu^2.$$

If n is taken equal to the Avogadro number 6.06×10^{23}, $\frac{1}{2}\, mnu^2$ represents the total kinetic energy of 1 mol of the gas, and we have

$$pv = 2/3 \text{ kinetic energy of 1 mol.} \tag{29}$$

$$\text{Kinetic energy} = 3/2\, pv.$$

But $$pv = RT = 2\,T$$

therefore, $$\text{kinetic energy of 1 mol} = 3\,T \text{ cal.} \tag{30}$$

If $3\,T_2$ represents the kinetic energy at temperature T_2, and $3\,T_1$ at temperature T_1, the difference in kinetic energy is $3(T_2 - T_1)$ calories. If now the difference in temperature is made exactly 1° the difference in kinetic energy is 3 calories, and this value is the molar heat capacity at constant volume, C_v, because it is defined as the number of calories necessary to raise 1 mol of the gas through 1°. For monatomic gases

$$C_v = 3 \text{ cal. per degree.} \tag{31}$$

It has been found that monatomic gases have a molar heat capacity of 3 calories per degree in perfect agreement with this formula.

Since $C_v = 3$ for monatomic gases, and $C_p = C_v + 2$ (equation 25), it follows that $C_p = 5$, and

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.66. \tag{32}$$

Again, this relation is in excellent agreement with the experimental facts.

In the case of polyatomic molecules the heat energy supplied is used not only in increasing the kinetic energy of translation in the three directions but also in increasing the energy of rotation and of vibration of the atoms within the molecule. If the extra energy absorbed is represented by a, then the ratio of the two specific heats will be

$$\gamma = \frac{C_p}{C_v} = \frac{5 + a}{3 + a} < 1.66 > 1. \tag{33}$$

The ratio becomes less than 1.66 in this case and with increasing complexity of the molecule the value of a increases and the ratio γ becomes continuously smaller, but it cannot become less than 1.

There is nothing in equation (31) to indicate that the heat capacity

of a monatomic gas is affected by temperature but in the equation for polyatomic gases it can be seen that, if a changes with temperature, both the heat capacities and their ratios may be influenced by a temperature change. As a matter of fact, the molar heat capacity of monatomic gases is found to be 3 calories per degree at all temperatures but the heat capacity of polyatomic gases increases with increasing temperature. In some cases the relation is given simply by the following empirical equation*

$$C_p = 6.5 + bT, \tag{34}$$

where b is a constant for each gas. The value of b for hydrogen, nitrogen, and carbon monoxide is 0.001; for ammonia, 0.0071; and for carbon dioxide, 0.0084. As the complexity of the gas increases the value of b becomes greater.

The extra energy a absorbed by polyatomic molecules becomes less as the temperature is lowered, and in the case of hydrogen γ becomes 1.66 below 100° absolute. These facts are of interest in connection with the quantum theory and they will be discussed more fully in Chap. XXIV.

In the following table some heat capacities are given, and it will be

MOLAR HEAT CAPACITIES OF GASES

Gas	Mc_p	Mc_v	$c_p/c_v=\gamma$
Argon	5.0	3.0	1.66
Helium	5.0	3.0	1.66
Mercury	5.0	3.0	1.66
Hydrogen	6.88	4.88	1.41
Oxygen	6.96	4.96	1.40
Nitrogen	6.93	4.93	1.41
Chlorine	8.58	6.58	1.36
Bromine	8.88	6.88	1.29
Nitric oxide	6.95	4.95	1.40
Carbon monoxide	6.86	4.86	1.41
Hydrochloric acid	6.68	4.68	1.41
Carbon dioxide	9.55	7.55	1.30
Nitrous oxide	9.94	7.94	1.30
Water	8.65	6.65	1.28
Sulphur dioxide	9.88	7.88	1.29
Ozone	....	....	1.29
Ether	27.80	25.80	1.08

* An empirical equation is one which expresses the facts but has no theoretical foundation. Such equations are useful in a practical way but they are less interesting from a theoretical standpoint.

seen that for monatomic gases $C_v = 3$ and $\gamma = 1.66$; that C_p is always greater than C_v by 2 calories per degree; and that the value of γ decreases as the molecule becomes more complex.

REFERENCES

The Kinetic Theory of Gases. Meyer. Translated by Baynes.
The Kinetic Theory of Gases. Loeb.
Treatise on Physical Chemistry. Taylor. Chapter III.

PROBLEMS

1. (*a*) The volume of a quantity of gas is measured when the barometer stands at 720 mm., and is found to be 646 cc. What will the volume be at normal pressure?
(*b*) At what pressure will it have a volume of 580 cc.?
Ans. (*a*) 612 cc. (*b*) 801.9 mm.

2. A given quantity of gas at 25° and 735 mm. pressure is found to have a volume of 607 cc. What will the volume be when reduced to standard conditions?

3. At what temperature will the volume of a given mass of gas be double what it is at 17°? *Ans.* 307°.

4. Using the expression $pv = nRT$ calculate the volume occupied by 100 g. of ammonia at 100° and 720 mm. The molecular weight of ammonia is 17.03.

5. A liter of air weighs 1.293 g. under standard conditions. At what temperature will a liter of air weigh 1 g., the pressure being 72 cm.? *Ans.* 61.43°.

6. (*a*) How many grams are there in a liter of carbon dioxide at 2 atmospheres and 200°?
(*b*) How many molecules?

7. 34.23 cc. of a certain gas (phosphine) at 20° and 700 mm. weighs 0.0447 g. What is the molecular weight of the gas? *Ans.* 34.1.

8. How many molecules are there in a liter flask containing air at 25°, which has been evacuated to 0.001 mm. pressure?

9. Calculate the molecular weight of chloroform from the following data obtained with a Victor Meyer apparatus. Weight of chloroform taken = 0.220 g. Volume of air collected over water = 45.0 cc. Temperature of air = 20.0°. Barometric pressure = 755.0 mm. Vapor pressure of water at 20° = 17.4 mm. *Ans.* 121.1.

10. Calculate the molecular weight of ethyl bromide from the following data obtained with a Victor Meyer apparatus. Weight of ethyl bromide = 0.3056 g. 68.4 cc. of air was expelled over water at 20.2° C. at which temperature the vapor pressure of water is 17.6. The atmospheric pressure was 744.2 mm.

11. 0.7160 g. of an organic compound of empirical formula C_2H_3O gave 327.6 cc. of vapor at 200° C. and 750 mm. pressure. What is the molecular formula of the compound? *Ans.* $C_4H_6O_2$.

12. A compound having the empirical formula CH has a vapor density of 2.550 g. per liter at 100° C. and 760 mm. What is the molecular formula of the compound?

13. (*a*) The density of a gas is 0.23 referred to mercury vapor. What is the molecular weight? *Ans.* 46.1.
(*b*) A certain gas is 1.377 times as heavy as oxygen. What is its molecular weight?
(*c*) A liter of air weighs 14.48 times as much as a liter of hydrogen at the same temperature and pressure. What is the average "molecular weight" of air?

14. Calculate x in the table on page 21.

15. Using the data given in the table on page 21 calculate the volume occupied by 100 g. of nitrogen tetroxide when partially dissociated at 25° and 1 atmosphere pressure.

16. 2.3253 g. of nitrogen tetroxide at 22.9° exerts a pressure of 440.6 mm. when vaporized and partially dissociated in a bulb of 1296 cc. capacity. To what extent is the gas dissociated under these conditions?

17. Phosphorous pentachloride dissociates according to the equation, $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The molecular weight of PCl_5 is 208.30. At 182° the partially dissociated gas is 73.5 times as heavy as hydrogen; at 203° it is 62 times as heavy. What is the degree of dissociation at 182°; at 203°? *Ans.* $\alpha_{182°} = 0.406$.

18. At 1000° the vapor of bromine is 4.8 times as heavy as oxygen. What is the degree of dissociation of diatomic molecules of bromine into single atoms at this temperature?

19. The time of outflow of a gas through a small opening is 21.4 minutes and the corresponding time for hydrogen is 5.6 minutes. What is the molecular weight of the gas? *Ans.* 29.4.

20. What is the molecular weight of a gas which escapes through an opening in 13.5 minutes, if hydrogen at the same temperature and pressure requires 2.39 minutes?

21. If a liter of oxygen diffuses through a small crack in an apparatus in one hour, how long will it take a liter of helium to diffuse through under the same conditions?

22. The times of effusion of equal volumes of air and carbon dioxide are 36.9 seconds and 45.3 seconds respectively. The average "molecular weight" of air is 28.95. Calculate the molecular weight of carbon dioxide. *Ans.* 43.6.

23. What is the average velocity of oxygen molecules at 25°?

24. What is the average velocity of molecules in steam at 100° C.

25. The specific heat at constant volume for argon is 0.075 and its molecular weight is 40. How many atoms are there in the molecule?

26. Mercury vapor is monatomic. How many calories of heat are required, at constant pressure, to raise 10 g. of mercury vapor through 1° C.?

Throughout the book and in all problems temperatures refer to the Centigrade scale unless otherwise stated. Sometimes C. is specified but usually it is not. Absolute temperature is designated by K. (for Kelvin scale). T refers to absolute temperature and t to Centigrade temperature.

CHAPTER III

LIQUIDS

General Characteristics of Liquids. A liquid has no definite shape but it does retain a definite volume under given conditions. The distance between molecules is much less in liquids than in gases as illustrated by the fact that one mol of water at its normal boiling-point occupies 18 cc. but when vaporized it occupies over 30,600 cc. This closer proximity of the molecules in the liquid state results in a lesser fluidity and lesser effects from temperature and pressure changes. The energy in the liquid state is less than in the gaseous state because energy is always absorbed in separating molecules in a liquid.

There is no fundamental difference in nature between the liquid and the gaseous state and in fact the distinction between the two becomes lost at the critical temperature. The critical temperature is the temperature above which the gas cannot be liquefied no matter how much pressure is applied. The pressure required to liquefy the gas at the critical temperature is the critical pressure, and the volume occupied by a mol of the gas or liquid under these conditions is the critical volume.

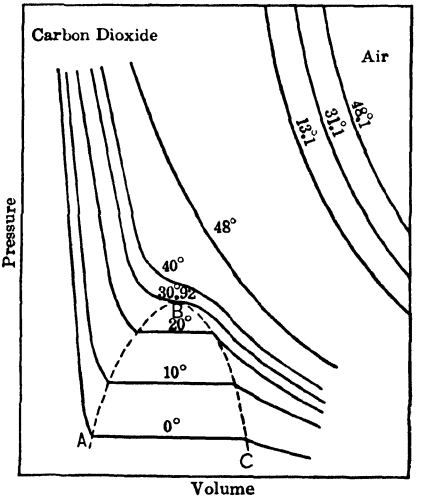


FIG. 7

Isothermals of Carbon Dioxide. The results of Andrews' experiments* on the liquefaction of carbon dioxide are shown in Fig. 7, in which the ordinates represent pressures, and the abscissas the corresponding volumes, at constant temperature. The curves obtained by plotting volumes against pressures at constant temperatures are called *isothermals*. For a gas which follows Boyle's law, the isothermals will be a series of right-angled hyperbolas. This condition is approximately fulfilled by air,

* Trans. Roy. Soc., **159**, 583 (1869).

for which three isothermals are given in the diagram. At 48° the isothermal for carbon dioxide is nearly hyperbolic, but as the temperature becomes lower, the isothermals deviate more and more from those for an ideal gas. At the critical temperature, 30.92°, the curve is almost horizontal for a short distance, showing that for a very slight change in pressure there is an enormous shrinkage in volume. At still lower temperatures, 20° and 10°, the horizontal portions of the curves are much more pronounced, indicating that during liquefaction there is no change in pressure. When liquefaction is complete, the curves rise abruptly, showing that the change in volume is extremely small for a large increase in pressure; in other words the liquefied gas possesses a small coefficient of compressibility. At any point within the parabolic area, indicated by the dotted line ABC, both vapor and liquid are coexistent; at any point outside, only one form of matter, either liquid or vapor, is present.

Van der Waals' Equation and the Continuity of the Gaseous and Liquid States. In the preceding chapter we have learned that the fundamental gas equation, for one mol,

$$pv = RT,$$

is strictly applicable only to an ideal gas, and that the behavior of actual gases is represented with considerable accuracy, even at high pressures, by the equation of van der Waals (p. 14),

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

If this equation is arranged in descending powers of v, we have

$$v^3 - v^2\left(b + \frac{RT}{p}\right) + v\frac{a}{p} - \frac{ab}{p} = 0.$$

This is a cubic equation and has three possible solutions, each value of p affording three corresponding values of v; a, b, R and T being treated as constants. The three roots of this equation are either all real, or one is real and two are imaginary, depending upon the values of the constants. That is to say, at one temperature and pressure the values of a and b may be such, that v has three real values, while at another temperature and pressure, v may have one real and two imaginary values. In the accompanying diagram, Fig. 8, a series of graphs of the equation for different values of T is given. It will be observed that these curves bear a striking resemblance to the isotherms of carbon dioxide established by the

experiments of Andrews. In the case of the theoretical curves there are no sudden breaks such as appear in the actual discontinuous passage from the gaseous to the liquid state. Instead of passing from B to D along the wavelike path $BaCbD$, experiment has shown that the substance passes directly from the state B to the state D along the straight line BD. It is here that van der Waals' equation fails to apply. As has been pointed out, the substance between these two points is not homogeneous, being partly gaseous and partly liquid. However, by studying supersaturated vapors and superheated liquids, it has been found possible to follow the theoretical curve for short distances between B and D without discontinuity, but owing to the instability of the substance in this region, it is evident that the complete isothermal and continuous transformation of a gas into a liquid cannot be effected. Attention has been called by van der Waals to the fact that, in the surface layer of a liquid, where unique conditions prevail, it is quite possible that such unstable states may exist, and that there the transition from liquid to gas may in reality be a continuous process. The diagram shows that as T increases, the wavelike portion of the isothermals becomes less pronounced and eventually disappears, when the points B, C and D coalesce. The substance at this point is in the critical condition. Since under these conditions the three roots of the equation,

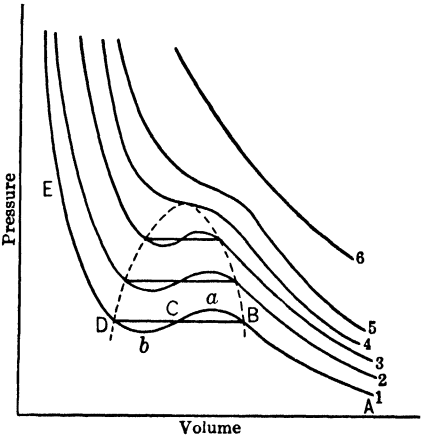


FIG. 8

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{a}{p_c}v - \frac{ab}{p_c} = 0, \qquad (1)$$

are equal, we may write $v_1 = v_2 = v_3 = v_c$, the subscript c indicating the critical state. Then equation (1) must be equivalent to

$$(v - v_c)^3 = v^3 - 3\,v_c v^2 + 3\,v_c^2 v - v_c^3 = 0. \qquad (2)$$

Equating the coefficients of v in (1) and (2)

$$3\,v_c^2 = \frac{a}{p_c}, \qquad (3)$$

and equating the constant terms

$$v_c^3 = \frac{ab}{p_c}. \tag{4}$$

It is possible then to determine the values of the constants, a and b, for any gas from a knowledge of the critical volume and critical pressure for

$$a = 3\, p_c v_c^2 \tag{5}$$

and

$$b = v_c/3 \tag{6}$$

as is evident by dividing equation (4) by equation (3).

Equating the coefficients of v^2 in a similar manner and substituting the values of v_c and p_c, it can be shown that

$$R = \frac{8}{3}\frac{p_c v_c}{T_c} \tag{7}$$

Obviously a and b and R must be expressed in the same units as p and v, usually in cubic centimeters and atmospheres.

In the following table the value of van der Waals' constants, a and b, are given for several gases, together with the pressures at 0° C. calculated according to van der Waals' equation and according to the ideal gas law. In each case one mol of the gas is contained in the volume designated, and for comparison, the experimentally determined pressures are included.

CALCULATED AND OBSERVED PRESSURES OF ONE MOL OF GAS AT 0° C.

Gas	a atm.×cc.^{2}	b (cc.)	Volume (cc.)	$p_{expt.}$	$p_{calc.}$ ($pv=RT$)	Deviation (per cent)	$p_{calc.}$ (van der Waals)	Deviation (per cent)
CO_2	3.61×10^6	42.8	22,400	0.9932	1	0.68	0.9946	0.14
			224,000	0.0993	0.1	0.07	0.0993	0.0
O_2	1.36×10^6	31.6	22,400	0.9992	1	0.08	0.9987	−0.05
			224,000	0.1000	0.1	0 00	0.09997	−0.03
H_2	0.19×10^6	23	22,400	1.0007	1	−0.07	1.0006	−0.01
			224,000	0.10002	0.1	−0.02	0.10000	−0.02
			2,240	10.06	10	−0.6	10.07	+0.1
			448	51.60	50	−3.2	51.59	−0.02
SO_2	6.69×10^6	56.5	22,400	0.9759	1	+2.41	0.9892	+1.33

It will be observed that van der Waals' equation gives values which are in close agreement with the observed pressures. It will

be noted too that the gases become more nearly ideal at the lower pressures; that is, they agree better with the equation $pv = RT$.

Corresponding States. If, in the equation of van der Waals, the values of p, v and T are expressed as fractions of the corresponding critical values, representing the fractions as α, β and γ, we may write

$$p = \alpha p_c,$$

$$v = \beta v_c,$$

and

$$T = \gamma T_c.$$

Substituting these values in the equation

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

we have

$$\left(\alpha p_c + \frac{a}{(\beta v_c)^2}\right)(\beta v_c - b) = R\gamma T_c, \tag{8}$$

and replacing a, b and R by their values given in equations (5), (6) and (7), we obtain

$$\left(\alpha + \frac{3}{\beta^2}\right)(3\beta - 1) = 8\gamma, \tag{9}$$

which is known as van der Waals' *reduced equation of state.*

In this equation everything connected with the individual nature of the substance has vanished, thus making it applicable to all substances in the liquid or gaseous state in the same way that the fundamental gas equation is applicable to all gases, irrespective of their specific nature. It has been shown, however, that the equation is not entirely trustworthy and at best can be considered as little more than a rough approximation.

The chief point to be emphasized is that gases may be compared through their equations of state under any conditions, but liquids must be compared at their critical temperatures or at equal fractions of their critical temperatures, i.e., in corresponding states. The experiments of Young* confirm the conclusion of van der Waals that when the absolute temperatures of two liquids are proportional to their critical temperatures their vapor pressures also are proportional to their critical pressures and their volumes are proportional to their critical volumes. A practical application of this relation is discussed later on p. 87.

Berthelot's Equation. Numerous modifications of the equation of van der Waals have been proposed from time to time, but of these

* Phil. Mag., (5), **33**, 153 (1892).

only one need be considered here. As has already been pointed out, a well-defined relation is known to exist between the constants a and b of any particular gas and its critical constants. An equation derived by D. Berthelot,* in which a and b are expressed in terms of the critical constants, has been found to represent the behavior of pure gases with a high degree of accuracy over an extended range of pressures. Berthelot's equation may be written in the following form: —

$$pv = RT\left[1 + \frac{9}{128}\frac{p}{p_c}\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]. \tag{10}$$

In this equation p_c and T_c are the critical pressure and the critical temperature, respectively. Inspection of the equation shows that as T increases or as p decreases, it approaches the simple equation, $pv = RT$, expressing the behavior of an ideal gas. The values of the ratio, pv/RT, calculated by means of equation (10), agree closely with those determined experimentally, provided the gases are neither associated nor dissociated, and that they are sufficiently removed from their critical points.

The most important application of Berthelot's equation is in the precise determination of atomic weights by the physical method (see p. 14). The approximate value of the molecular weight M, of g grams of any gas may be calculated by the equation

$$M = g\frac{RT}{pv}, \tag{11}$$

or, since $d = g/v$, where d is the density of the gas, equation (11) may be written in the form

$$M = d\frac{RT}{p}. \tag{12}$$

If we wish to determine the exact molecular weight of a gas, however, it is necessary to introduce a correction for the deviation from the gas laws. To do this, we make use of the equation of Berthelot instead of the simple equation, $pv = RT$, and obtain the equation

$$M = d\frac{RT}{p}\left[1 + \left\{\frac{9\ T_c(T^2 - 6\ T_c^2)}{128\ p_c T^3}\right\}p\right], \tag{13}$$

or, letting A denote the expression within braces, we have

$$M = d\frac{RT}{p}(1 + Ap). \tag{14}$$

* J. Phys., (3), **8**, 263 (1899).

This value of the molecular weight, M, is so accurate that the exact atomic weights can be calculated. This method of calculating exact atomic weights is known as the " method of critical constants."

Limiting Density. Owing to the fact that the deviation from the simple gas laws becomes less and less as the pressure is lowered, it is evident that the exact value of the molecular weight of a gas can also be calculated directly from its density, provided this can be determined in the neighborhood of zero pressure. The determination of this so-called " limiting density " can be made with a high degree of accuracy, if the density of the gas at low pressures is known, or if it can be obtained by extrapolation to low pressures.

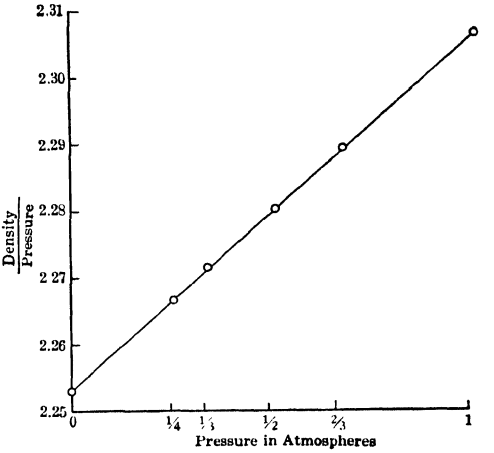


FIG. 9

As the pressure decreases the volume increases and the density d or g/v decreases but g/pv changes only slightly. If the gas is ideal, the product of pressure and volume, pv, is constant and $\frac{g}{pv}$ is the same at all pressures. If the gas is not ideal, it becomes more nearly ideal at the lower pressures because the mutual attractions of the molecules are less and the volumes of the molecules themselves become comparatively negligible. Under these conditions the molecular weight may be determined accurately from density measurements but the experimental difficulties involved in weighing a large volume of gas at low pressures are great. In the following table are given the densities and the values of $\frac{d}{p}$ for methyl chloride determined at different pressures at 0° C., and in Fig. 9 $\frac{d}{p}$ is extrapolated to zero pressure giving a value of 2.2527.

This is the value of $\frac{g}{pv}$ under conditions where the simple gas law holds with precision and the molecular weight M is given accurately by the equation

$$M = \frac{g}{pv} RT.$$

Substituting in this equation, the molecular weight of methyl chloride is found to be 50.488 and subtracting the atomic weights of carbon and three hydrogens the atomic weight of chlorine is 35.465.

MOLECULAR WEIGHT OF METHYL CHLORIDE

Pressure (atmospheres)	Density at 0° C. (grams per liter)	$\frac{\text{Density}}{\text{Pressure}}$ at 0° C.
1.000	2.3074	2.3074
0.666	1.5263	2.2895
0.500	1.1401	2.2802
0.333	0.75713	2.2714
0.250	0.56660	2.2664
0	....	(2 2527)

If the deviations from the ideal gas law are slight, it can be assumed that they are directly proportional to the pressure and an extrapolation to zero pressure may be effected without graphing.

Liquefaction of Gases. Among the first workers to liquefy gases was Faraday.* He liquefied practically all the gases which condense under moderate pressures and at not very low temperatures. The apparatus used by Faraday consisted of an inverted V-shaped tube, in one end of which was placed some solid which would liberate the desired gas on heating, while the other end was sealed and immersed in a freezing mixture. When the substance had been heated long enough to liberate considerable gas, the pressure became sufficiently high to cause the gas to liquefy at the temperature of the other end of the tube. Thus, when chlorine hydrate was heated in the tube, the liberated chlorine condensed as a yellow liquid.

In 1834, Thilorier† succeeded in liquefying carbon dioxide in quite large amounts by the use of a new form of apparatus. In connection with his experiments on liquid carbon dioxide, he observed that, when it was allowed to vaporize, enough heat was absorbed to lower the temperature below its freezing-point, solid carbon dioxide being obtained. He discovered that a mixture of solid carbon dioxide and ether was a powerful refrigerant, and that under diminished pressure the mixture gave temperatures ranging from − 100° C. to − 110° C. This mixture is known today as *Thilorier's mixture.*

In 1895, Linde in Germany and Hampson in England simultaneously and independently constructed machines for the liquefaction

* Phil. Trans., **113**, 189 (1823).

† Lieb. Ann., **30**, 122 (1839).

of air in large quantities. In the Linde liquefier, the air is compressed to about 200 atmospheres. It is then passed through a chamber containing anhydrous calcium chloride to remove the greater part of the moisture, after which it is cooled by allowing it to circulate through a coiled pipe immersed in a freezing mixture. Nearly all the moisture remaining in the air is deposited on the walls of the pipe in the form of frost. The air then enters a long spiral tube jacketed with a non-conducting material, and is there allowed to expand to a pressure of about 15 atmospheres. During this expansion the temperature of the air is appreciably lowered. When the air has traversed the spiral tube, it is still further cooled by allowing it to expand to a pressure equal to that of the atmosphere. The air which has been thus cooled is then passed backward through the annular space between the spiral tube and a concentric jacket, thus cooling the entering portion of air. Consequently this next portion of air expands from a lower initial temperature, and the cooling effect is increased. In like manner, when this cooler air passes backward it cools still further the next succeeding portion, and eventually the temperature is reduced sufficiently to cause a small amount of the air to liquefy as it issues from the end of the spiral tube. The remaining portion of the air, which has not been liquefied, passes backward through the annular tube and cools the following portion to a still greater extent, causing a larger proportion to liquefy on expansion. With a 3-horse-power machine, a continuous supply of about 1 liter per hour can be obtained. Further improvements in this apparatus were made by Dewar and Hampson.

The most efficient apparatus for the liquefaction of air and other gases is that developed by Claude. The essential features of his liquefier are shown in Fig. 10. The air is first compressed to 40 atmospheres pressure by means of an ordinary compression pump not shown in the diagram, the moisture and carbon dioxide being removed with suitable reagents. It then enters the tube A, which in reality is of a spiral form, and divides at B. A portion enters the cylinder D through a valve chest similar to that in a steam engine, forcing out the piston and causing the wheel, W, to revolve, thereby doing work and simultaneously cooling the air. The cooled air escapes from the valve chest and circulates through the liquefying chamber L, where it causes the portion of compressed air entering at B to liquefy. It then issues from the liquefier and traverses M, cooling the entering portion of air in A, and finally returns to the compressor. The pressure of the air when it issues from D is almost atmospheric, but its temperature is below $-140°$ C. About 25 per

cent of the power consumed in compression is regained by the motor. The apparatus produces about 1 liter of liquid air per horse-power hour. By means of this improved apparatus, based upon the regenerative principle, all known gases have now been liquefied. Helium, the last to succumb, was liquefied, in 1908, by Kammerlingh Onnes in the Leyden cryogenic laboratory. The subjoined table gives the critical data, together with the boiling and freezing temperatures, of some of the more common gases.

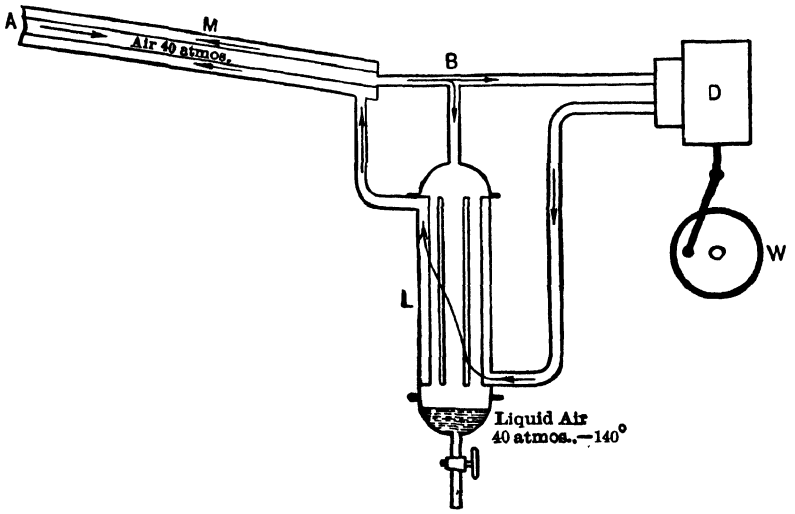


FIG. 10

The following principles are involved in the liquefaction of gases: (1) the gas must be below its critical temperature; (2) the pressure must be great enough to cause liquefaction, and the lower the temperature the lower is the required pressure; (3) the incoming gas is cooled by the outgoing gas which has been cooled by expansion; (4) the gas is cooled by doing external work in an engine; and (5) by expanding against the small internal force of attraction between the molecules.

The Linde process makes use only of the cooling due to this expansion of air against molecular attraction, corresponding to the a in van der Waals' equation, and in spite of its extensive use in this country it is very inefficient from a theoretical standpoint. Instead of allowing the energy of compression to be wasted by free expansion into the atmosphere it should be conserved by passage of the expanding gases through an engine as in the Claude process. In operating an expansion engine at low temperatures, however, there are practical

difficulties of lubrication and unequal thermal contraction of the moving parts.

PHYSICAL CONSTANTS OF SOME OF THE PRINCIPAL GASES

Gas	grams/liter 0° 760 mm.	d_c grams/cc.	M.P. °K	B.P. °K	T_c °K	P_c atmos.
He	0.1785	0 0693	<0.9	4.2	5.2	2.26
H_2	0.08988	0.0310	13.96	20.4	33.2	12.8
Ne	0.9002	0.484	24.43	27.2	44.4	25.9
N_2	1.25057	0.3110	63.2	77.3	126.0	33.5
CO	1.250	0.311	66.1	81.1	134.1	35
O_2	1.4290	0.430	54.7	90.1	154.3	49.7
A	1.7832	0.531	83.9	87.4	151.1	48
NO	1 3402	0.52	112.1	122.1	179.1	65
CH_4	0.717	0.162	89.1	111.7	190.6	45.8
Kr	3.71	0.78	104 1	121.3	210.1	54
Xe	5.85	1.155	133.1	164 0	289.7	58.2
CO_2	1.9769	0.460	....	194.6	304 2	73.0
HCl	1.6392	0.42	162.1	188.1	324.5	81.6
NH_3	0.7710	0.235	195.4	239.7	405.5	111.5
Cl_2	3.214	0.573	171.5	238.5	417.1	76.1
SO_2	2.9269	0.52	200.4	263.1	430.3	77.7
H_2S	1.539	....	190.2	213.5	373.5	88.9
PH_3	1.529	0.30	140.6	185.7	324.1	64

The liquefaction of gases finds extensive application in refrigeration. Ammonia, sulphur dioxide and methyl chloride are commonly used. A new refrigerant, solid carbon dioxide, known as "dry ice," is now finding many technical uses. Many gas mixtures can be separated by liquefaction and the fractional distillation of liquid air is the chief source of commercial nitrogen and oxygen. If the cost of liquefying air could be reduced, many new uses for oxygen would arise, particularly in combustion operations involving the production of high temperatures.

Separation of Helium from Natural Gas. No treatment of the liquefaction of gases, however brief, should be concluded without mention of the distinctively American industry of separating helium from natural gas on a commercial scale.

Early in the present century the presence of small amounts of the rare gases in certain of the natural gases of Kansas was discovered by Cady. Because of its lightness, non-inflammability and low rate of diffusion through fabrics, helium is an ideal gas for the inflation of balloons and the gas bags of dirigibles. The demand for large

quantities of this rare gas for aëronautical purposes furnished the necessary stimulus for the development of processes whereby the small amounts of helium present in various sources of natural gas could be separated on a commercial scale. A typical sample of one of these natural gases has the composition shown in the following table: —

	Per cent
Helium	0.93
Carbon dioxide	0.25
Oxygen	0.54
Methane	56.85
Ethane and heavier hydrocarbons	10.30
Nitrogen	31.13
	100.00

The process of separation involves the liquefaction of all the gases present in the mixture except the helium, followed by a process of purification of the latter in which the percentage of helium is increased from about 70 to over 90 per cent. In the Claude process, which is one of several different processes employed, the natural gas is taken from the gas-holder at atmospheric pressure and led through a train of scrubbers to remove the carbon dioxide. The gas then enters the separators in which a large proportion of the moisture is removed. From the separators it is led to the compressor where the pressure is raised to approximately 600 lb. per sq. in. The gas then passes through the coolers where the heat developed by compression is removed and then at atmospheric temperature it enters the oil removers. After the removal of the oil, it passes through a battery of driers containing granular calcium chloride to remove the last traces of moisture. The gas now enters the heat interchangers where the incoming current of gas meets the returning previously cooled gas. After traversing the interchangers, 25 per cent of the gas is run through a liquefier, while the other 75 per cent is expanded through a small expansion engine from the initial 600 lb. pressure down to 120 lb. The gas which issues from the expansion engine is partially liquefied after traversing a train of condensers, the last member of which is cooled by the expansion of a mixture of liquefied methane and nitrogen. The last traces of methane are practically completely removed at this point as well as a large proportion of the nitrogen. The helium together with the residual unliquefied nitrogen is then collected in a large reservoir from which it can be subsequently removed for purification.*

* An excellent detailed account of the commercial preparation of helium is given by Dr. R. B. Moore, J. Franklin Inst., **191**, 145 (1921).

Vapor Pressure of Liquids. According to the kinetic theory there is a continuous flight of particles of vapor from the surface of a liquid into the free space above it. At the same time the reverse process of condensation of vapor particles at the surface of the liquid is taking place. Eventually a condition of equilibrium will be established between the liquid and its vapor, when the rate of escape will be exactly counterbalanced by the rate of condensation of vapor particles: the vapor is then said to be *saturated.* The pressure ex-

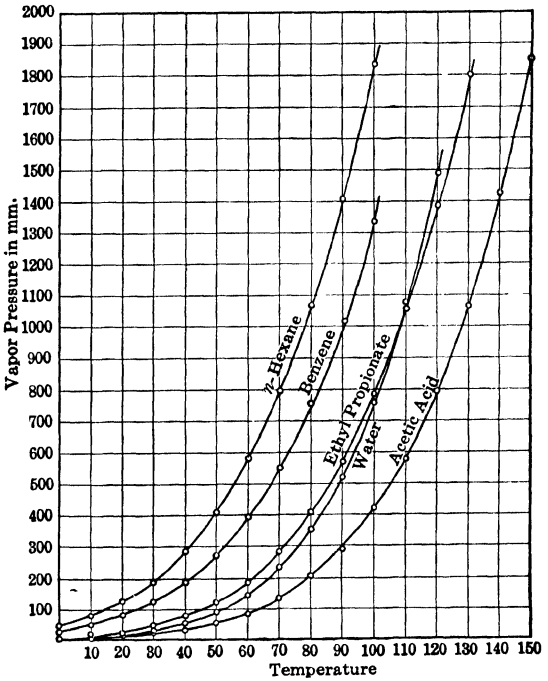


FIG. 11

erted by the vapor which is in equilibrium with the liquid phase is known as the *vapor pressure.* The equilibrium between a liquid and its vapor is dependent upon the temperature. For every temperature below the critical temperature, there is a certain pressure at which vapor and liquid may exist in equilibrium in all proportions; and conversely, for every pressure below the critical pressure, there is a certain temperature at which vapor and liquid may exist in equilibrium in all proportions. This latter temperature is termed the boiling-point of the liquid in the special case where the pressure is 760 mm. The vapor pressure of a liquid is a constant quantity at

any temperature and is independent of the amounts of liquid and vapor present but it increases as the temperature is raised. The following table gives the vapor pressures of several typical liquids from 0° to 100° C.

VAPOR PRESSURES

Temp., °C.	Water	Acetic Acid	Ethyl Propionate	*n*-Hexane	Benzene
0	4.579	....	8.3	45.4	26.5
10	9.209	....	15.5	75.0	45.4
20	17.535	11.7	27.7	120.0	74.7
30	31.824	20.6	....	185.4	118.2
40	55.324	34.8	77.9	276.7	181.1
50	92.51	56.6	....	400.9	269.0
60	149.38	88.9	188.0	566.2	388.6
70	233.7	136.0	....	787.0	547.4
80	355 1	202.3	403.6	1062	735.6
90	525.76	293.7	...	1407	1016.1
100	760.00	417.1	785.0	1836	1344.3

The data of the foregoing table are represented graphically in Fig. 11.

Relation between Vapor Pressure and Temperature. The first attempt to correlate vapor pressure and temperature was made by Dalton, who suggested that the vapor pressure of a liquid increases in geometrical progression as the temperature increases in arithmetical progression.

A more satisfactory relation, proposed by Young, has the form

$$\log p = A + B/T, \tag{15}$$

where A and B are constants and T is the absolute temperature. If two different substances have the same vapor pressure, p, at the two absolute temperatures, T' and T'' respectively, it follows from equation (15) that

$$\log p = A' + B'/T' = A'' + B''/T'', \tag{16}$$

or

$$\frac{T'}{T''} = \frac{1}{B''}[B' + (A' - A'')T']. \tag{17}$$

It is apparent that the ratio of the absolute temperatures, at which the two substances have the same vapor pressure, is a linear function of the temperature T' of one of the substances. If the constants, A and B, of a standard substance are evaluated by measuring its vapor

pressure at two different temperatures, Ramsay and Young have shown that equation (17) may be employed to deduce the vapor pressure of an unknown substance.

Probably the most accurate of the many empirical vapor-pressure formulas which have been proposed is that first derived by Kirchhoff* in 1858, and subsequently by Rankine in 1866. This equation, sometimes known as the Kirchhoff formula and more often as the Rankine formula, may be written in the form,

$$\log p = \frac{A}{T} + B \log T + C, \tag{18}$$

where A, B and C are constants. This formula has been found to apply to a large variety of substances up to the critical temperature with a maximum error not exceeding 3 per cent.

An inspection of equations (15) and (18) reveals the fact that the logarithm of the vapor pressure of a liquid is very nearly a linear function of the reciprocal of its absolute temperature. The validity of this statement is borne out by the curves shown in Fig. 12 which represent the logarithms of the vapor pressures, given in the table and Fig. 11, plotted as functions of the reciprocals of the corresponding absolute temperatures.

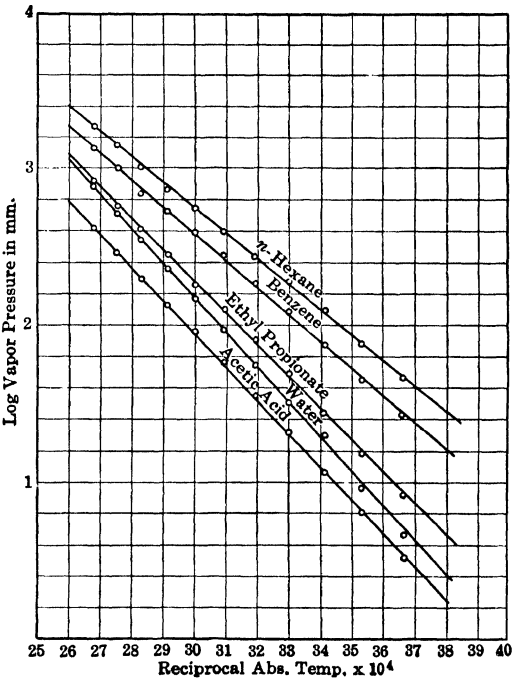


FIG. 12

Measurement of Vapor Pressure. The vapor pressure of a liquid may be measured directly by placing a portion of it above the mercury in the vacuum of a barometer tube, heating to the desired temperature, and observing the depression of the mercury column. This is known as the *static method.* It is open to the objection that the

* Kirchhoff, Pogg. Ann., **103**, 185 (1858).

presence of volatile impurities in the liquid causes too great depression of the mercury column, the vapor pressure of the impurity adding itself to that of the liquid whose vapor pressure is sought. A better method for the measurement of vapor pressure is that known as the *dynamic method.* In this method, the pressure is maintained constant and the boiling temperature is determined with an accurate thermometer. The boiling temperatures corresponding to various pressures may be measured, provided we have a suitable device for changing and measuring the pressure. The results obtained by the static and dynamic methods agree closely if the liquid is pure, but if volatile impurities are present the results obtained by the dynamic method are more trustworthy. A method for the measurement of vapor pressure due to James Walker* is of considerable interest. In this method, a current of pure dry air is bubbled through a weighed amount of the liquid whose vapor pressure is to be determined. The liquid is maintained at constant temperature and its loss in weight is observed. In passing through the liquid, the air will absorb an amount of vapor directly proportional to the vapor pressure of the liquid. If v is the volume of gas which contains g grams of the vapor of the liquid whose molecular weight is M, and p is the vapor pressure of the liquid at the temperature T, then

$$pv = \frac{g}{M} RT, \tag{19}$$

or

$$p = \frac{g}{Mv} RT. \tag{20}$$

In this equation, v denotes the total volume containing g grams of the liquid in the form of vapor, or in other words it represents the air and vapor together. Since the volume of the air is, in general, so much greater than that of the vapor, v may be taken as that of the air alone, when the vapor pressure is low.

Other methods for measuring vapor pressure will be considered in Chapter VIII.

Law of Cailletet and Mathias. If the densities of a liquid and its saturated vapor are plotted against temperature, a curve of the form shown in Fig. 13 is obtained. This curve shows that as the temperature is raised the densities of the liquid and vapor phases approach each other and, at the critical temperature, become equal. Cailletet and Mathias† pointed out that the mean of the densities of

* Z. physik. Chem., **2**, 602 (1888).

† Compt. rend., **102**, 1202 (1886); **104**, 1563 (1887).

any substance in the state of liquid and saturated vapor, when plotted against the corresponding temperatures, lie on a straight line. If d_l and d_v denote the densities of liquid and vapor respectively, the relation of Cailletet and Mathias may be expressed mathematically by the equation,

$$\frac{d_l + d_v}{2} = a + bT, \quad (21)$$

where a and b are constants. This relation is sometimes called the law of the *rectilinear diameter*. It holds fairly well for a number of substances, but with others it is found that the mean of the densities of the two phases is not strictly a linear function of the temperature. In general it may be said that the relation holds in the immediate vicinity of the critical temperature better than at lower temperatures. The law of Cailletet and Mathias has proven useful in determining the value of the critical density, a quantity which frequently cannot be measured directly.

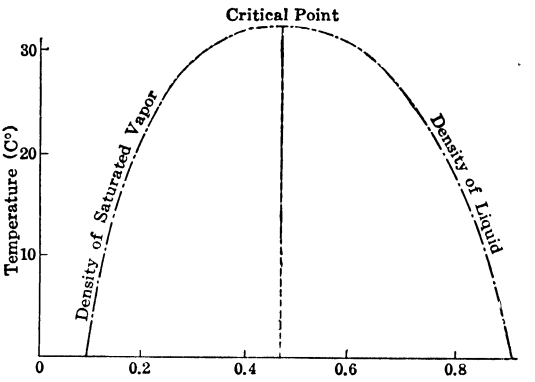


FIG. 13

RELATION OF BOILING-POINT TO CRITICAL TEMPERATURE

Substance	T_b	T_c	T_b/T_c
Oxygen	90°	154°	0.58
Chlorine	239°	417°	0.58
Sulphur dioxide	263°	430°	0.61
Ethyl ether	308°	467°	0.66
Ethyl alcohol	351°	516°	0.68
Benzene	353°	562°	0.63
Water	373°	647°	0.58
Phenol	454°	692°	0.66

Boiling-Point and Critical Temperature. An interesting relation has been pointed out by Guldberg* and Guye.† These two investigators have shown that the absolute boiling temperature

* Z. physik. Chem., **5**, 376 (1890).

† Bull. Soc. Chim., (**3**), **4**, 262 (1890).

of a liquid is about two-thirds of its critical temperature. That this empirical relation holds for a variety of different substances is shown in the accompanying table.

The Law of Ramsay and Young. It was pointed out by Ramsay and Young* that if the absolute boiling-points of two closely related liquids, A and B, are compared under equal pressures, the following relation, which may be derived from equation (17), will be found to hold: —

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} + c(T'_A - T_A), \tag{22}$$

where T_A and T_B are the absolute boiling-points of A and B under the same pressure, T'_A and T'_B the corresponding boiling-points under another pressure, and c is a constant. This relation has been shown to be valid from very low pressures up to the critical pressure. The constant c is practically zero for the majority of closely related liquids. The law of Ramsay and Young has been found very useful in estimating the values of the boiling-points of different liquids over a range of pressures, the corresponding variation in boiling-point of a closely related liquid being taken as a standard of comparison. Furthermore, variation in the value of the constant c may be used as a criterion of abnormality in the molecular state of liquids.

Heat of Vaporization. In order to transform a liquid into a vapor, a large amount of heat is required. Thus, when a liquid is vaporized at the boiling-point, the volume must be increased against the pressure of the atmosphere, but much more energy is expended in overcoming intermolecular attraction. The heat required to convert 1 gram of a liquid at the boiling-point into vapor at the same temperature is known as the heat of vaporization of the liquid.

Undoubtedly the most satisfactory method for the determination of heats of vaporization is that developed by Mathews.† In this method the amount of electrical energy required to vaporize a given weight of the liquid is accurately measured and the equivalent in thermal units is calculated.

The apparatus is shown in Fig. 14. The vaporizer B containing the pure liquid is suspended by a wire from the arm of an analytical balance directly above the apparatus. Two heavy platinum wires sealed into the base of the vaporizer serve as terminals of the heating coil L and make contact with the electrical circuit through long mercury cups I. The vaporizer hangs freely in the jacket A, which

* Phil. Mag., (5), **20**, 515 (1885); **21**, 33 (1886); **22**, 37 (1886).

† J. Am. Chem. Soc., **48**, 562 (1926).

is heated by boiling some of the same liquid in the lower reservoir with the electric heating coil H. The cap C is attached to the jacket with a ground-glass joint. A second jacket D resting in a mercury channel in a cork permits the recovery of the material in the condenser F. Condensation of liquid on the suspension wire is prevented by the small heating coil E and by the passage of dry air.

In carrying out a determination, the liquid in the jacket is boiled until the liquid in the vaporizer is brought to its boiling-point and then a current of exactly 1 ampere is passed through the coil L, slight variations in the current being eliminated by careful operation of an external rheostat. The potential drop across the heating coil is measured carefully with a potentiometer, and the time is measured with a chronometer. These three measurements of current, voltage and time permit a calculation of the energy input, and the design of the apparatus insures that all this energy is expended in evaporating the liquid in the vaporizer. A 1-gram weight is removed, and as the liquid is vaporized the pointer of the balance swings back toward zero. The chronometer is started when the pointer passes the zero mark and it is stopped when it passes the zero mark again after removing a 10-gram weight from the balance pan.

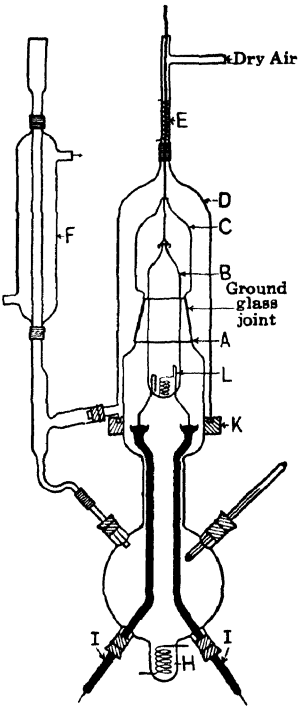


FIG. 14

Dissolved air is boiled out before the experiment is started and the whole of the liquid is conserved with the help of the condenser. In any exact measurements of this kind it is very essential to use only highly purified liquids.

Trouton's Relation. An interesting relation between the heat of vaporization and the absolute boiling-point of a liquid was discovered by Trouton.* If T denotes the absolute boiling-point, and l_v the heat of vaporization of 1 gram of liquid whose molecular weight is M, then according to Trouton,

$$\frac{Ml_v}{T} = 21, \tag{23}$$

* Phil. Mag., (5), **18**, 54 (1884).

or in words, the ratio of the molar heat of vaporization to the absolute boiling temperature of a liquid is constant, the numerical value of the ratio being approximately 21. This is known as Trouton's rule. While this relation holds quite well for many liquids, Nernst has pointed out that the constant varies with the temperature, and has proposed two other forms of the equation. Bingham has simplified the equations of Nernst to the following form: —

$$\frac{Ml_v}{T} = 17 + 0.011\ T. \tag{24}$$

More exact relations which are useful in industrial work, particularly in the refining of oil, have been reviewed and developed by Watson.*

These relations do not hold unless the substance has the same molecular weight in the gaseous and liquid state. For example in the liquid state, water is thought to be *associated* or polymerized and these molecular complexes are broken down when the liquid is vaporized. The reaction

$$(H_2O)_n \rightarrow n\ H_2O$$

absorbs a considerable amount of heat which must be added to the normal heat of vaporization. The exact value of n is often unknown and the interpretation of associated liquids given here is not entirely satisfactory. Liquids such as water, ammonia and alcohols have abnormally large heats of vaporization and possess other abnormal properties, also. They are called polar compounds indicating that there is an unbalanced electrical condition. The non-polar compounds such as hydrogen, carbon tetrachloride and benzene, on the other hand, possess heats of vaporization and other properties which can often be calculated from general formulas.

The Internal Pressure of Liquids. The importance of allowing for the existence of attractive forces acting between the molecules of gases becomes more and more evident as the pressure is increased. As has been pointed out, the term a/v^2 was introduced by van der Waals into the equation expressing the simple gas laws to correct for this intermolecular attraction. If such attractive forces did not exist, it is obvious that much larger pressures would be required to bring about the liquefaction of gases than is actually the case. For example, it may be shown that if no attractive forces were operative between the molecules of water vapor, the pressure required to condense 1 gram-molecule of vapor into the volume occupied by 1 gram-molecule of liquid water, at room temperature, would be over 1300 atmospheres. The pressure required to condense 1 gram-molecule

* Ind. Eng. Chem., **23**, 360 (1931).

of a substance in the gaseous state to the volume occupied by 1 gram-molecule in the liquid state, in the absence of intermolecular attraction, is called the *internal pressure* of the liquid. The ultimate cause of intermolecular attraction is still a matter of conjecture and, although numerous equations have been derived for the calculation of the internal pressure of liquids, the results thus far obtained are not entirely satisfactory. The following table gives the values of the internal pressure of a few liquids.

INTERNAL PRESSURE OF LIQUIDS*

Substance	Int. Press. (atmos.)
Mercury	13,050
Carbon tetrachloride	3640
Benzene	4050
Carbon disulphide	5400

Surface Tension. The attraction between the molecules of a liquid manifests itself near the surface where the molecules are subject to an unbalanced force. The molecules at the surface are pulled inward by the other molecules of the liquid and the liquid tends to adjust itself to give the minimum surface area. This fact explains many common phenomena, including the spherical shape of raindrops, the rise of water in a capillary tube and the movement of water in blotting paper or in the soil.

Some liquids, like water, wet the walls of a glass capillary tube whereas others, like mercury, do not. When the liquid wets the tube, the liquid adhering to the walls pulls the body of the liquid up and decreases the total surface area, but when the liquid does not adhere, the liquid is depressed. In the first instance the surface of the liquid in the tube is concave. In the second it is convex. The surface area in every case tends toward a minimum.

The most accurate method for determining the surface tension of a liquid consists in measuring the height to which it rises in a capillary tube.

Let a capillary tube of radius r, as shown in Fig. 15, be immersed in a vessel of liquid whose density is d, and let the elevation of the liquid in the capillary be denoted by h. The downward force exerted by the column of liquid in the capillary is $\pi r^2 hdg$, where g is the accelera-

* Hildebrand, J. Am. Chem. Soc., **41**, 1071 (1919); **43**, 500 (1921). Int. Crit. Tables **IV**, 19.

tion due to gravity. The force sustaining this weight is the vertical component, $2\pi r\gamma \cos\theta$, of the force due to the tension of the liquid surface at the walls of the tube, γ being the surface tension and θ the angle of contact of the liquid surface with the walls of the tube.

Therefore

$$\pi r^2 hdg = 2\pi r\gamma \cos\theta, \qquad (25)$$

or

$$\gamma = \frac{hdgr}{2\cos\theta}. \qquad (26)$$

In the case of water and many other liquids θ is so small that we may write $\theta = 0$, and $\cos\theta = 1$, and the foregoing expression becomes

$$\gamma = 1/2\, hdgr. \qquad (27)$$

Thus the surface tension of a liquid can be calculated provided its density and the height to which it rises in a previously calibrated tube are known. When h and r are expressed in centimeters, γ will be expressed in dynes per centimeter or ergs per square centimeter.

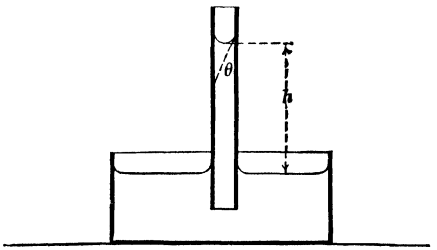


FIG. 15

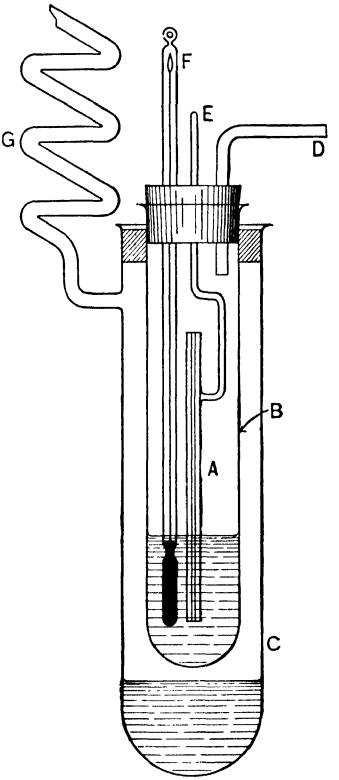


FIG. 16

A simple form of apparatus* for the determination of surface tension is shown in Fig. 16. A capillary tube A of uniform bore is sealed to a glass rod E, which is held in position in the test tube B by means of a cork stopper. A short right-angled tube D and a thermometer F are also passed through the same cork stopper. The liquid whose surface tension is to be measured is introduced into the tube B, the cork inserted and the tube placed inside of the larger tube C containing a liquid of known boiling-point. When the thermometer F has become stationary, the capillary elevation of the liquid is measured with a cathetometer. The tube D permits the escape of vapor from

* Getman, Am. Chem. Jour., **44**, 145 (1910).

the liquid in *B* and at the same time insures equality of pressure inside and outside of the apparatus. The spiral tube *G* serves as an air condenser, preventing loss of vapor from the liquid in the outer tube.

It has been demonstrated by Richards and Coombs,* that the values of the surface tension of liquids, as determined by the capillary method, are in error, owing to the fact that the values of h, in equation (27), as ordinarily measured, are slightly less than the true values of h, when measured from a strictly horizontal surface. To avoid this source of error, Richards and Coombs devised the apparatus shown in Fig. 17, where the larger tube has a sufficient diameter (38 mm.) to secure a perfectly flat surface. The height to which a liquid rises in the capillary tube is measured by means of a cathetometer; the difference between the reading of the telescope when focused, (1) on the capillary meniscus, and (2) on the horizontal surface in the wide tube, is the true capillary rise, h.

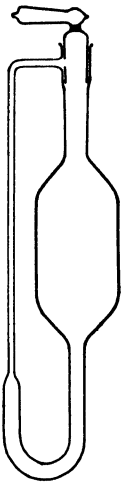


FIG. 17

Surface Tension and Temperature. The surface tension of a liquid has been found to depend upon the nature of the liquid and also upon its temperature. In 1886, Eötvös† showed that the surface tension multiplied by the two-thirds power of the molecular weight and specific volume is a function of the absolute temperature, or

$$\gamma(Mv)^{\frac{2}{3}} = f(T),$$

where γ is the surface tension, M the molecular weight, v the specific volume or reciprocal of the density, and T the absolute temperature. Ramsay and Shields‡ modified the equation of Eötvös as follows: —

$$\gamma(Mv)^{\frac{2}{3}} = k(t_c - t - 6), \qquad (28)$$

t_c being the critical temperature of the liquid, t the temperature of the experiment, and k a constant independent of the nature of the liquid. The physical significance of the two-thirds power of the molar volume has been explained by Ostwald in the following manner: — Assuming the molecules to be spherical, we shall have for two different liquids, the proportion

$$\frac{V_2}{V_1} = \frac{r_2^3}{r_1^3},$$

* J. Am. Chem. Soc., **37**, 1656 (1915). † Wied. Ann., **27**, 448 (1886)
‡ Z. physik. Chem., **12**, 431 (1893).

where V_1 and V_2 represent the volumes and r_1 and r_2 the radii of their respective molecules. Similarly the ratio of the surfaces, S_1 and S_2, of the molecules in terms of their respective radii, will be

$$\frac{S_1}{S_2} = \frac{r_1^2}{r_2^2}.$$

From these two proportions it follows that the ratio of the molecular surfaces in terms of the molecular volumes, will be

$$\frac{S_1}{S_2} = \frac{V_1^{\frac{2}{3}}}{V_2^{\frac{2}{3}}}.$$

Equation (28) is useful for calculating the surface tension at different temperatures, and the values of the critical temperatures obtained with it are in close agreement with those obtained by other methods.

Making use of the value of M as determined in the gaseous state, Ramsay and Shields found the value of k for a large number of liquids to be 2.12 when the surface energy is expressed in ergs. Among the liquids for which this value of k was found were benzene, carbon tetrachloride, carbon disulphide and phosphorus trichloride. For certain other liquids such as water, methyl and ethyl alcohols, and acetic acid k was found to have values much smaller than 2.12. Ramsay and Shields attributed these abnormalities to an increase in molecular weight due to association and calculated values for the molecular weights assuming that k has the value of 2.12. There is, however, legitimate doubt as to the theoretical significance of the so-called molecular weight in the liquid state.

Although the capillary-rise method is perhaps the standard method for determining surface tensions, several others have been used successfully. The simplest method involves a measurement of the force necessary to pull a wire ring from the surface of a liquid.* Morgan† and Harkins‡ have developed the drop-weight method to a high degree of accuracy. The weight of a drop which falls away from the tip of a burette depends on the surface tension of the liquid. A special tip is required and many drops are counted, collected and weighed. The influence of temperature is given by the formula

$$w(Mv)^{\frac{2}{3}} = k'(t_c - t - 6), \tag{29}$$

where w is the average weight of a drop and the other symbols have the same significance as in equation (28).

* Du Noüy, J. Gen. Physiology, (**1**), **5**, 521 (1919).

† J. Am. Chem. Soc., **33**, 349 (1911).

‡ J. Am. Chem. Soc., **38**, 246 (1916).

Viscosity. The resistance experienced by one portion of a liquid in moving over another portion is called *viscosity*. The viscosity of liquids varies greatly, some liquids, such as ether, being very mobile, while others, such as tar, are extremely viscous. It has been shown experimentally that the tangential force, f, required to maintain a constant difference between the velocities of two parallel layers of liquid moving in the same direction varies directly with the difference in velocity, u, and the area, A, of the surface of contact of the two layers, and inversely as the distance, d, between the layers. That is,

$$f = \eta \frac{Au}{d}, \tag{30}$$

where η is a proportionality factor known as the *coefficient of viscosity*. The unit of viscosity is the *poise;* it is a viscosity such that unit force per unit area causes two parallel liquid surfaces of unit area and unit distance apart to slide past one another with unit velocity. The viscosity of a liquid is generally measured by observing the time required for a definite volume of liquid to flow through a standardized capillary tube under a known difference of pressure. The law governing the flow of liquids through capillary tubes was discovered by Poiseuille* and may be expressed by the equation

$$\eta = \frac{\pi P r^4}{8 V l} t, \tag{31}$$

in which V denotes the volume of liquid of viscosity η, flowing through a capillary tube of length l, and radius r, in the time t, and under the pressure P. If the times of flow of equal volumes of two liquids through the same capillary are measured under the same head of liquid, it follows from equation (31) that

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}, \tag{32}$$

where η_1 and η_2 denote the coefficients of viscosity of the two liquids, d_1 and d_2 their densities and t_1 and t_2 their times of flow. If a liquid of known viscosity is selected as a standard, equation (32) may be used to calculate the so-called "relative viscosity" of other liquids. Water is quite generally accepted as the standard of reference in determinations of relative viscosity. In calculating the relative viscosity of a liquid referred to water, therefore, we employ the following equation:

$$\frac{\eta_1}{1} = \frac{d_1 t_1}{d_w t_w}, \tag{33}$$

* Ann. chim. phys., **37**, 50 (1843).

in which η_1, d_1 and t_1 denote the viscosity, density and time of flow, respectively, of the liquid under investigation, and d_w and t_w denote the density and time of flow of water. Relative viscosities may be transformed into absolute viscosities by multiplying the relative viscosity by the absolute viscosity of water at the same temperature as that at which the measurements are made. At 25° the absolute viscosity of water is 0.00895 poise.

A convenient type of viscometer is shown in Fig. 18. The liquid is allowed to flow under its own pressure through the capillary *db*. An accurately measured volume of the liquid is introduced at *f*, and by applying suction at *a* it is drawn up the tube until the liquid has risen above the mark *c*. The liquid is now allowed to flow down the tube, and the time required for the meniscus to move from the mark *c*, to the lower mark *d*, is measured with a stop-watch. The experiment is now repeated with the same volume of water after which the viscosity of the liquid can be calculated by means of equation (33).

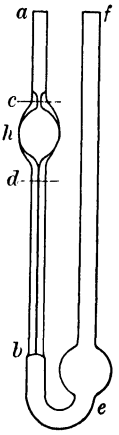


FIG. 18

The reciprocal of viscosity is called *fluidity*, i.e., $\phi = 1/\eta$. Fluidity may be regarded as a measure of the tendency of a liquid to flow, whereas viscosity is a measure of the resistance which a liquid offers to flowing.

The viscosity of liquids has been found to decrease about 2 per cent for each degree rise in temperature. Increase of pressure, on the other hand, causes the viscosity of liquids to increase, the change in viscosity corresponding to equal increments of pressure being greater at high pressures than at low.

While there appears to be an abundance of experimental evidence to prove that the viscosity of a mixture of two or more liquids is not equal to the sum of the viscosities of the components, it is claimed by Bingham that there is both theoretical and experimental justification for the statement that fluidities are additive. He points out that the fluidity ϕ of a mixture of two liquids whose fluidities are ϕ_1 and ϕ_2, respectively, may be represented by the equation

$$\phi = a\phi_1 + b\phi_2, \tag{34}$$

where a and b denote the volume concentrations of the two liquids. This equation has been found to hold in the case of liquids which are "inert," i.e., liquids which are not only individually non-associated but also exhibit no tendency to combine with each other.

Numerous applications of viscometric methods to various problems in both pure and applied chemistry might be cited. Thus, they have

proven valuable in the study of such problems as keto-enol tautomerism, the determination of the order of chemical reactions, the existence of racemates in solution and the determination of transition points. In biology and physiology the viscometer has become an almost indispensable instrument for the study of the properties of blood and other animal fluids, and in the realm of technology it has been successfully applied to the solution of a wide variety of problems presented by the paint, rubber, glue, textile, and other industries.

Plasticity. As has been pointed out in a previous paragraph, the law governing the flow of liquids through capillary tubes was discovered by Poiseuille and is expressed mathematically by equation (31). This equation may be re-arranged as follows: —

$$\text{Velocity of flow} = \frac{V}{t} = \left(\frac{\pi r^4}{8\,\eta l}\right) P. \tag{35}$$

From this expression it is apparent that the velocity of flow is proportional to the driving pressure. This type of flow is termed *viscous flow* and is to be differentiated from another type of flow exhibited by plastic solids, known as *plastic flow*.* Plastic flow differs from viscous flow in that an initial pressure P_0 is necessary to start it, whereas in the case of viscous flow no such initial impulse is required.

An example is found in a suspension of clay particles in water. At low concentrations the particles slip by each other and viscous flow is obtained, but at higher concentrations the particles stick together and form bridges which are broken only after the application of a definite minimum pressure, i.e., plastic flow is exhibited.

The velocity of plastic flow is proportional to the difference between the normal driving pressure P and the initial starting pressure P_0. The distinction between viscous flow and plastic flow becomes clear when we compare the following equations expressing the velocity of the two types of flow: —

$$\text{Velocity of viscous flow} = \frac{V}{t} = k_v P, \tag{36}$$

$$\text{Velocity of plastic flow} = \frac{V}{t} = k_v(P - P_0). \tag{37}$$

For very high and very low values of $P - P_0$ the latter equation fails to hold, presumably owing to slippage of the material through the viscometer.

* Further information is given in J. Phys. Chem., **29**, 1201–1282 (1925).

REFERENCES

Stoichiometry. Young.
The Viscosity of Liquids. Dunstan and Thole.
Fluidity and Plasticity. Bingham.
Surface Equilibria of Biological and Organic Colloids. Du Noüy.

PROBLEMS

1. The critical temperature of ammonia is 130° and the critical pressure is 115 atmospheres. Calculate the critical volume and calculate van der Waals' constant b in cc. Calculate van der Waals' a in atmospheres.

Ans. $v_c = 107.9$ cc. $b = 36.0$ cc.
$a = 4.013 \times 10^6$ atmos.

2. For ether $t_c = 193.8$ and $p_c = 2706$ cm. of mercury. Evaluate van der Waals' constants a (in atmospheres) and b (in *cc.*).

3. Calculate the pressure exerted by a mol of sulphur dioxide in 10 liters at 100° using (*a*) ideal gas law, (*b*) van der Waals' equation, (*c*) Berthelot's equation.

4. Calculate the volume of 453.6 g. (one pound) of ammonia at 1 atmosphere and −40° C. using (*a*) ideal gas law, (*b*) Berthelot's equation.

5. The density of nitric oxide at 0° and 760 mm. is 1.3402 g. per liter. What is the molecular weight of nitric oxide, calculated by Berthelot's equation? What is the atomic weight of nitrogen from these data?

6. The weight of 1 liter of radon at 0° and 1 atmosphere would be 9.93 g. The critical pressure is 62.4 atmospheres, the critical temperature is 104.4° K (absolute scale). What is the atomic weight of radon?

7. The ratio of the weight of 1 liter of methyl fluoride, CH_3F, to the pressure in atmospheres at three different pressures is as follows: 1.54507 at 760 mm., 1.53576 at 506.67 mm. and 1.52665 at 253.33 mm. Calculate the molecular weight of methyl fluoride and the atomic weight of fluorine by the method of limiting densities. The temperature of the measurements was 0°. *Ans.* $CH_3F = 34.012$; $F = 18.99$.

8. The density of ammonia in grams per liter was determined at various pressures by weighing the gas in large glass bulbs. The values of d/p (d = density in grams per liter at 0°, p = pressure in atmos.) were as follows: 0.77169 at 1 atmosphere, 0.76773 at $\frac{2}{3}$ atmosphere, 0.76585 at $\frac{1}{2}$ atmosphere, 0.76383 at $\frac{1}{3}$ atmosphere. What is the limiting value of density/pressure at zero pressure and what is the molecular weight of ammonia? Taking the atomic weight of hydrogen as 1.008 what is the atomic weight of nitrogen?

9. The critical temperature of normal pentane is 197°.15. The orthobaric densities of normal pentane in the liquid and vapor states at several temperatures are as follows:

Temp.	d_l	d_v	Temp.	d_l	d_v
110°	0.5248	0.0203	180°	0.3867	0.0935
130	0.4957	0.0310	190	0.3445	0.1269
150	0.4604	0.0476	195	0.3065	0.1609

Plot the data and find the equation of the straight line which passes through the average densities $\frac{(d_1 + d_2)}{2}$. Solve this equation for the density at the critical temperature.

10. The vapor pressure of benzene is as follows: 45.43 at 10.0°, 181.08 mm. at 40.0°, 547.4 mm. at 70.0°. Plot the logarithm of the vapor pressure against the reciprocal of the absolute temperature and determine the constants for the equation of the best straight line which passes through the three points. Calculate the vapor pressure at 0° and 25°. *Ans.* $\log p = \frac{-1750}{T} + 7.85$.

11. The vapor pressures of iodobenzene are as follows: 13.65 mm. at 70.0°, 73.88 mm. at 110.0°, and 479.7 mm. at 170.0°. Plot the logarithm of the vapor pressure against the reciprocal of the absolute temperature, and find a linear equation for the graph. What is the vapor pressure at 0°; at 100°?

12. Ten liters of air passed through ethanol at 0.0° C. caused the evaporation of 0.335 g. of the liquid. What is the vapor pressure of the ethanol in atmospheres? In mm. of mercury? Mol. wt. ethanol = 46.05.

13. Twenty liters of air was bubbled through brombenzene (molecular weight = 156.96) at 30°. The loss in weight of the liquid was 0.9503 g. What is the vapor pressure?

14. How many grams of water vapor is contained in a room 10 m. × 5 m. × 3 m., at 25° C., when the relative humidity is 50 per cent? The vapor pressure of water at this temperature is 23.7 mm. (Relative humidity = partial pressure water vapor, divided by vapor pressure of the liquid water.)

15. How many liters of dry air is required to evaporate 1000 g. of water at 25° where the vapor pressure is 23.7 mm.; at 0° where the vapor pressure is 4.6 mm.?

16. Estimate the boiling-points of three organic liquids, from the molecular weights using Trouton's rule. Compare the estimated boiling-points with the observed boiling-points.

17. Calculate the surface tension of benzene from the fact that liquid benzene having a density of 0.85 rises 3.213 cm. in a capillary tube, which has a radius of 0.01843 cm. *Ans.* 24.69 dynes per cm.

18. Normal hexane has a surface tension of 18.43 dynes, and a density of 0.660 at 20°. What is the largest capillary which will cause the liquid to rise 1.5 cm.?

19. At 14.8° acetyl chloride (density = 1.124) ascends to a height of 3.28 cm. in a capillary tube the radius of which is 0.01425 cm. At 46.2° in the same tube the elevation is 2.85 cm. and the density is 1.064. What is the critical temperature of acetyl chloride? *Ans.* 234.9°.

20. The density of hexane at 20.0° is 0.660 and that of water is 1.000. Hexane flows through a viscometer in 76.1 seconds and the same volume of water under the same conditions requires 153.2 seconds. Calculate the relative viscosity and the absolute viscosity of hexane at 20°. The viscosity of water at 20° is 0.01009 poise.

Ans. 0.328 (relative)
0.00331 poise (absolute).

21. At 20° the density of chloroform is 1.523 and the viscosity 0.00563 poise. The density of ethanol is 0.789 and the viscosity 0.0171 poise. Under a given pressure, 10 cc. of chloroform requires 1 minute and 35 seconds to pass through a capillary tube. Under the same conditions how long will it take 10 cc. of ethanol to pass through?

CHAPTER IV

SOLIDS

General Properties of Solids. Solids differ from gases and liquids in possessing whatsoever form has been given them. The force of attraction between molecules or atoms in the solid state is greater than that which exists between molecules within gases or liquids and, accordingly, solids possess considerable mechanical strength and rigidity.

When a liquid is cooled sufficiently, it passes into the solid state; and when a solid is heated, it may pass into the liquid (or gaseous) state. The heat of fusion is the number of calories required to melt 1 gram of a solid, and the molar heat of fusion is the number required to melt a gram-molecule.

Although the units of a solid are rigidly bound together they are moving about within restricted regions with random motion at all temperatures above absolute zero. Some molecules at the surface attain sufficient velocity to break away from their neighboring molecules and pass into the gas phase. This transformation from the solid into the gas phase is called sublimation; it is analogous to the vaporization of a liquid. The sublimation pressure is the pressure on the gas phase when the solid is in equilibrium with its vapor.

It is often difficult to decide whether a substance should be classified as a solid or as a liquid. For example, the behavior of certain amorphous substances, such as pitch, amber and glass, is similar to that of a very viscous, inelastic liquid. Solids are generally classified as *crystalline* or *amorphous*. In crystalline solids the atoms are arranged in some definite order and this arrangement manifests itself in the crystal form. An amorphous solid on the other hand may be considered as a liquid possessing great viscosity and high rigidity. The physical properties of amorphous solids have the same values in all directions, whereas in crystalline solids the values of these properties may be different in different directions. When an amorphous solid is heated, it gradually softens and eventually acquires the properties characteristic of a liquid, but during the process of heating there is no definite point of transition from the solid to the liquid state. On the other hand, when a crystalline solid is heated

there is a sharp change from one state to the other at a definite temperature, this temperature being termed the *melting-point.*

Crystallography. The study of definite geometrical forms and properties of crystalline solids is termed *crystallography.* The number of crystalline forms known is exceedingly large, but it is possible to reduce the many varieties to a few groups or systems by referring their faces to definite lines called axes. These axes are so drawn

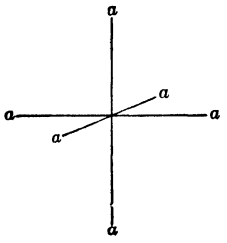


FIG. 19

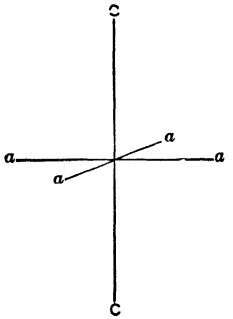


FIG. 20

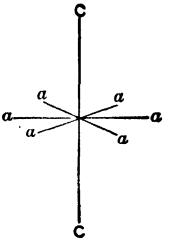


FIG. 21

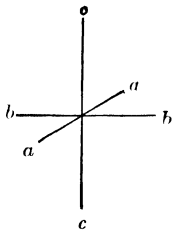


FIG. 22

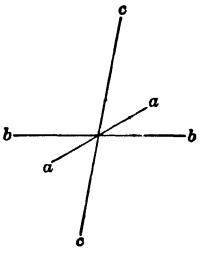


FIG. 23

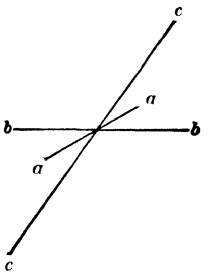


FIG. 24

within the crystal that the crystal surfaces are symmetrically arranged about them. This system of classification was proposed by Weiss in 1809. He showed that, notwithstanding the multiplicity of crystal habits encountered in nature, it is possible to consider them as belonging to one of six systems of crystallization.

The six systems of Weiss are as follows: —

1. *The Regular System.* Three axes of unit length, intersecting each other at right angles (Fig. 19).

2. *The Tetragonal System.* Two axes of unit length and the third axis either longer or shorter, all three axes intersecting at right angles (Fig. 20).

3. *The Hexagonal System.* Three axes of unit length, all in the same plane and intersecting at angles of 60°, and a fourth axis, either longer or shorter and perpendicular to the plane of the other three (Fig. 21).

4. *The Rhombic System.* Three axes of unequal length, all intersecting each other at right angles (Fig. 22).

5. *The Monoclinic System.* Three axes of unequal length, two of which intersect at right angles, while the third axis is perpendicular to one and not to the other (Fig. 23).

6. *The Triclinic System.* Three axes of unequal length no two of which intersect at right angles (Fig. 24).

The position of a plane in space is determined by three points in a system of coördinates, and consequently the position of the face of a crystal is likewise determined by its points of intersection with the three axes, or by the distances from the origin of the system of coördinates at which the plane of the crystal face intersects the three axes.

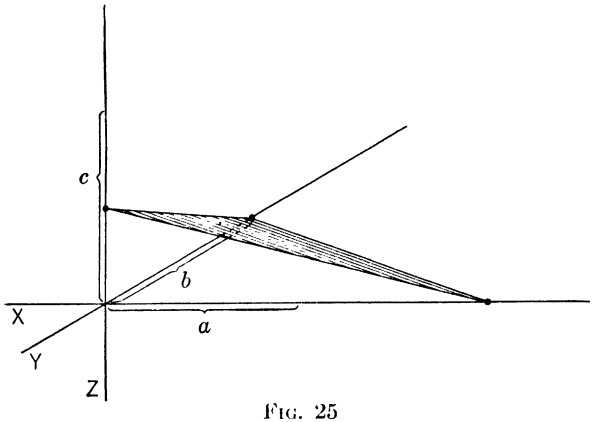


FIG. 25

Crystal Notation. Crystal faces are usually defined by their intercepts on the three axes in terms of the Miller indices devised in 1829. Unit distances along the X, Y and Z axes are termed a, b and c, respectively, and the Miller indices are obtained by taking the numerators of the reciprocals of the intercepts on the axes in terms of these unit distances after the reciprocals have been reduced to the lowest common denominator. In addition to the intercepts on the three crystallographic axes the angles between the axes must be specified. In the case of cubic crystals the axes are all at right angles and $a = b = c$.

Figure 25 shows the crystal axes X, Y, Z making angles of α, β and γ with one another and a plane cutting the X axis at 2 a, the Y axis at

b and the Z axis at $\frac{1}{2}$ c. The intercepts are 2, 1 and $\frac{1}{2}$, their reciprocals are $\frac{1}{2}$, 1 and 2, and the Miller indices are written 1, 2, 4. The reciprocals of the intercepts are multiplied so that no fractional numbers remain, the relative values of the intercepts being unaffected by the multiplication. The faces of crystals are usually of such a nature that the indices are small numbers, 1, 2, 3, 4, etc., or else they are parallel to the axis. In the latter case they cut the axis at ∞ and the Miller index is zero.

Crystal Angles. The fundamental law of crystallography, discovered by Steno in 1669, may be stated thus: — *The angle between two given crystal faces is always the same for the same substance at a given temperature.* The fact that a crystal is characterized by a constant interfacial angle, affords a valuable means of identification which is used by both chemists and mineralogists. The instrument employed for the measurement of the interfacial angles of crystals is called a *goniometer.* The crystal to be measured is mounted at the center of the graduated circular table of the goniometer, and the image of an illuminated slit, reflected from one surface of the crystal, is brought into coincidence with the cross-wires in the eye-piece of the telescope. The table is then turned until the image of the slit, reflected from the adjacent face of the crystal, coincides with the cross-wires. The interfacial angle of the crystal corresponds to the number of degrees through which the table has been turned.

Properties of Crystals. The properties of all crystals, except those belonging to the regular system, exhibit differences dependent upon the direction in which the particular measurements are made. Thus the elasticity, the thermal and electrical conductivities, and in fact all of the physical properties of crystals which do not belong to the regular system, have different values in different directions. Crystals whose physical properties have the same values in all directions are termed *isotropic,* while those in which the values are dependent upon the direction in which the measurements are made, are called *anisotropic.* Certain amorphous substances, such as glass, which are normally isotropic, may become anisotropic when subjected to tension or compression. The phenomenon of double refraction observed in all crystals, except those belonging to the regular system, is due to their anisotropic character. Crystals belonging to the tetragonal and hexagonal systems resemble each other in one respect, viz.: that in all of them there is one direction, called the optic axis (coincident with the principal crystallographic axis), along which a ray of light is singly refracted, while in all other directions it is doubly refracted. In crystals belonging to the rhombic,

monoclinic, and triclinic systems, there are always two directions along which a ray of light is singly refracted. A crystal of Iceland spar ($CaCO_3$) affords a beautiful illustration of double refraction. On placing a rhomb of this substance over a piece of white paper on which there is an ink spot, two spots will be seen. On turning the crystal, one spot will remain stationary while the other spot will revolve about it. This property of Iceland spar is utilized in the construction of Nicol prisms for polariscopes.

The examination of sections of anisotropic crystals in a polariscope between crossed Nicol prisms, reveals something as to their crystal form. As has been stated, crystals of the tetragonal and hexagonal systems are *uniaxial*. If a section is cut from such a crystal perpendicular to the optic axis, and this is placed between the crossed Nicol prisms of a polariscope, in a convergent beam of white light, a dark cross and concentric, spectral-colored circles, due to the interference of light, will be observed, Fig. 26. Upon turn-

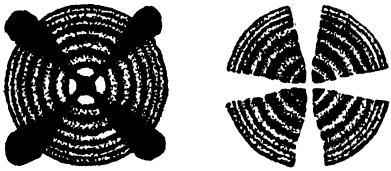


FIG. 26

FIG. 27

ing the analyzer through 90° the colors of the circles will change to the respective complementary colors and the dark cross will become light. Crystals of the rhombic, monoclinic, and triclinic systems are *biaxial*. If a section of a biaxial crystal, cut perpendicular to the line bisecting the angle between the two optic axes, is placed in the polariscope and examined as in the preceding case, a series of concentric spectral-colored lemniscates surrounding two dark centers and pierced by dark, hyperbolic brushes, will be observed, as shown in Fig. 27. On rotating the analyzer, the colors will change to the corresponding complementary colors, as in the case of uniaxial crystals. The appearance of these figures is so varied and characteristic as to furnish, in many cases, a very satisfactory means of identifying anisotropic crystals. Polarizing microscopes are widely used in analytical work, especially in soil analysis and in food analysis.

Etch Figures. The solubility of crystals has been shown to be different in different directions. Thus, if the surface of a crystalline substance is highly polished and then treated for a short time with a suitable solvent, faint patterns, known as *etch figures*, will appear as

a result of the inequality of the rate of solution in different directions. When these figures are examined under the microscope the crystal form can generally be determined. The examination of etch figures has come to be of prime importance to the metallographer. Thus, when an appropriate solvent is applied to the polished surface of an alloy, not only is the crystal form revealed by the etch figures, but also the presence of various chemical compounds may be recognized. By a careful study of the etch figures developed on the surface of highly polished metal, the metallographer may gather important information as to its previous history, especially its heat treatment.

In crime detection this technique has been helpful in proving with photomicrographs that a piece of metal came from a particular source. Also when the numbers stamped on a piece of metal have been filed smooth, it is frequently possible to reconstruct them by etching, the strains set up in the stamping process leading to unequal rates of reaction with the etching solution. Dilute nitric acid, picric acid and ammoniacal copper solution are among the etching solutions used for special purposes.

Crystal Form and Chemical Composition. From the preceding paragraphs it might be inferred that the same substance always assumes the same crystal form. Although this is true in general, there are many substances which appear in several different crystal forms. This phenomenon is termed *polymorphism.*

Calcium carbonate is an example of a substance crystallizing in more than one form. As calcite, it crystallizes in the hexagonal system; as aragonite, it crystallizes in the rhombic system. Such a substance is said to be *dimorphous.* Of the several factors controlling polymorphism, temperature is the most important. Thus sulphur crystallizes at temperatures above 95.6° in the monoclinic system, but at lower temperatures it assumes the rhombic form. The temperature at which it changes from one form into the other is termed its *transition temperature.*

If two substances crystallize in the same form with nearly identical angles, and can replace each other, they are said to be *isomorphous.* This phenomenon, discovered by Mitscherlich, was useful in connection with the earlier investigations on atomic weights.

X-Rays and Crystal Structure. Much light has recently been shed upon the question of the arrangement of the atoms and molecules within crystals by the interesting investigations which have been carried out on the transmission and reflection of X-rays by crystalline substances. It is a well-established fact that X-rays are in reality light waves of extremely short wave-length. The wave-length of the

X-ray is approximately 1×10^{-8} cm. and is of the same order of magnitude as the distance between contiguous atoms in crystals.

In 1912, Laue pointed out that the regularly arranged atoms of a crystal should act as a three-dimensional diffraction grating toward X-rays. He showed mathematically that, on traversing a thin section of a crystal, a pencil of X-rays should give rise to a diffraction pattern arranged symmetrically round the primary beam as a center. A photographic plate placed perpendicular to the path of the rays and behind the crystal should reveal, on development, a central spot due to the action of the primary rays, and a series of symmetrically grouped spots due to the diffracted rays.

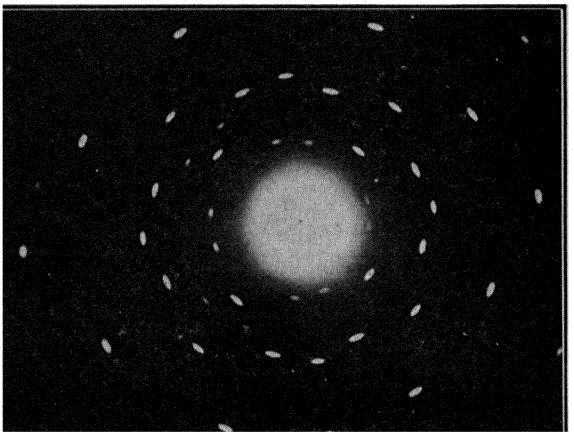


FIG. 28

Laue's predictions were verified experimentally by Friedrich and Knipping,* who obtained numerous plates showing a variety of geometrical patterns corresponding to the structural differences of the crystals examined. In Fig. 28, a Laue photograph of magnesium oxide is shown. The analysis of the Laue diffraction patterns, while furnishing valuable information as to the internal structure of crystals, is nevertheless extremely complex. In addition to the original method of Laue for the investigation of crystal structure, two other methods have been developed which have proved to be of great value.

Before entering upon a discussion of these methods, however, it may clarify the student's understanding of the subject if we digress to consider very briefly the possible geometrical arrangements of the structural units constituting a simple crystal.

* Ann. Physik, **41**, 971 (1913).

The Structure of a Cubical Crystal. Among the first crystalline substances studied by the method of X-ray analysis was sodium chloride, a compound which crystallizes in the cubic system. In the cubic system there are three possible arrangements or *space-lattices* of the fundamental structural units. These are known as the *simple cubic*, the *face-centered cubic* and the *body-centered cubic* lattices. It is convenient to regard the entire space-lattice as made up of an aggregation of cells among which the structural units of the

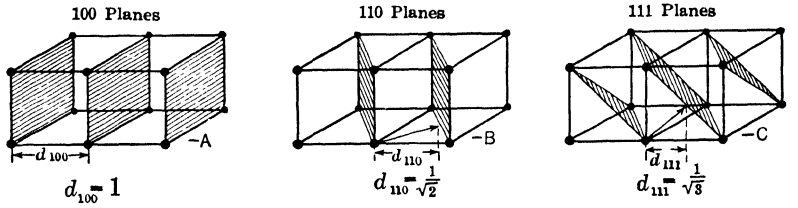


FIG. 29

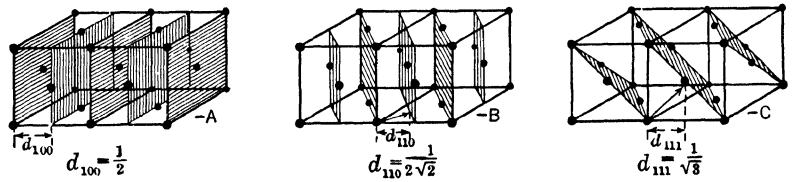


FIG. 30

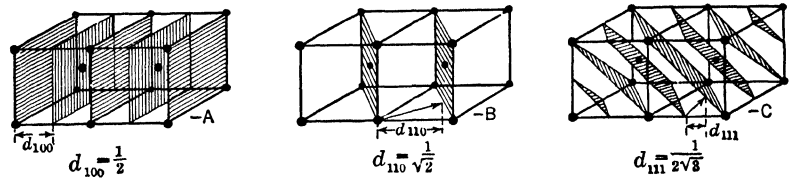


FIG. 31

macroscopic crystal are distributed. The three types of cells characteristic of the three cubic lattices are shown diagrammatically in Figs. 29, 30 and 31. It will be observed that in the simple cubic lattice, a single structural unit is situated at each corner of the cubic cell. In the face-centered lattice, there is one unit situated at each corner of the cubic cell and also one unit in the center of each face. In the body-centered lattice, there is one unit at each corner and also one unit at the center of the cubic cell.

In the cubic system there are three different ways in which planes can cut the axes, and the distance between these planes as determined by means of X-rays serves to identify the type of crystal.

In the *simple cubic lattice* shown in Fig. 29 *A* the (100) planes cut the *X* axis and are parallel to the *Y* and *Z* axes. In Fig. 29 *B* the (110) planes run obliquely across the *X* and *Y* axes but cut the *Z* axis at infinity, i.e., they are parallel to the *Z* axis. The Miller indices for such a plane are 1,1,0, as already explained. In Fig. 29 *C*, the planes cut obliquely across all three axes intercepting each at the same distance from the origin and giving the Miller indices 111. The distance between (100) planes, d_{100}, is obviously the length of a face or 1. The perpendicular distance between the (110) planes, d_{110}, is half the diagonal of a face or $\sqrt{2}/2$ or $1/\sqrt{2}$. The perpendicular distance between the 111 planes, d_{111}, is $1/\sqrt{3}$, a fact which can be demonstrated geometrically by taking proportional sides of similar triangles and finding that

$$\frac{d_{111}}{1} = \frac{1/\sqrt{2}}{\sqrt{1^2 + (1/\sqrt{2})^2}} = \frac{1/\sqrt{2}}{\sqrt{3/2}} = \frac{1}{\sqrt{3}}. \qquad (1)$$

In the face-centered cubic lattice additional (100) planes can be introduced as shown in Fig. 30 *A* by vertical shading. They pass vertically through the center of the front and back faces, and the distance between planes, d_{100}, is now 1/2 on the assumption that d_{100} for the simple lattice is 1. A new set of (110) planes also can be passed through the face-centered cubic lattice as shown in Fig. 30 *B*. These additional planes with vertical shading include the units in the centers of the front and side faces, and come midway between the planes of the simple cubic lattice. The distance between planes then is one-half as great as it is in the simple cubic lattice and d_{110} is $1/2 \times 1/\sqrt{2}$. The (111) planes of the simple lattice already pass through the centers of all the faces as shown in Fig. 30 *C*, and no new planes can be introduced. The distance between planes, d_{111}, is then the same as in the simple lattice, namely $1/\sqrt{3}$.

In the body-centered cubic lattice additional (100) planes can be passed through the units in the centers of the cube as indicated in Fig. 31 *A* with vertical shading. These new planes are half-way between the planes of the simple lattice, and $d_{100} = 1/2$. The (110) planes, as shown in Fig. 31 *B*, pass through the unit in the center of the cube and no new planes are possible. The value of d_{110} is then the same as it was in the simple cubic lattice, namely, $1/\sqrt{2}$. The (111) planes as shown in Fig. 31 *C* do not pass through the central units and it is possible to insert another set of planes through these units midway between the (111) planes of the simple lattice as shown with opposite shading. The distance between planes then is half as great and $d_{111} = 1/2 \times 1/\sqrt{3}$.

The ratios of the distances between the three different sets of planes in the three different types of cubes can now be summarized.

Simple cubic,

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}. \tag{2}$$

Face-centered cubic,

$$d_{100} : d_{110} : d_{111} = \frac{1}{2} : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}. \tag{3}$$

Body-centered cubic,

$$d_{100} : d_{110} : d_{111} = \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} = 1 : \frac{2}{\sqrt{2}} : \frac{1}{\sqrt{3}}. \tag{4}$$

The Bragg Method of X-Ray Analysis. W. H. Bragg and his son, W. L. Bragg,* showed that the diffraction of X-rays by the atoms of a crystal can be studied much more simply by employing the crystal as a reflection grating, rather than as a transmission grating, as in the method of Laue. The reflection of X-rays from the face of a crystal may be likened to the reflection of a beam of light from a bundle of thin glass plates of equal thickness. It is known that reflection from a bundle of plates will take place only at definite angles, the values of which will be dependent upon the wave-length of the incident light, as well as upon the thickness of the plates. The plates of glass correspond to the planes of atoms within the crystal, for the space-lattice arrangement of the structural units, or atoms, of a crystal is such that they are to be considered as lying in parallel planes, the orientation of which is determined by their indices and by the symmetry of the crystal. Each crystal face is developed parallel to one of these planes, the development favoring, as a general rule, those planes containing the maximum number of atoms.

A simple relation exists between the wave-length of the X-rays, the distance between atom planes in the crystal, and the angle of reflection. A similar formula was first derived for diffraction gratings ruled on glass surfaces.

In Fig. 32 the lines AM, BN and CO represent a series of parallel rays of monochromatic X-rays of wave-length λ. The horizontal lines represent a series of planes of atoms parallel to one face of the crystal and separated from each other by the distance d. The atoms in these planes become excited and emit secondary radiation which

* X-Rays and Crystal Structure.

gives rise to interference at an angle of reflection θ, equal to the angle of incidence. The radiation may be considered as reflected light.

AML represents the path of the light reflected from the first layer, BNL the path of the light reflected from the second layer, COL from the third, and so on.

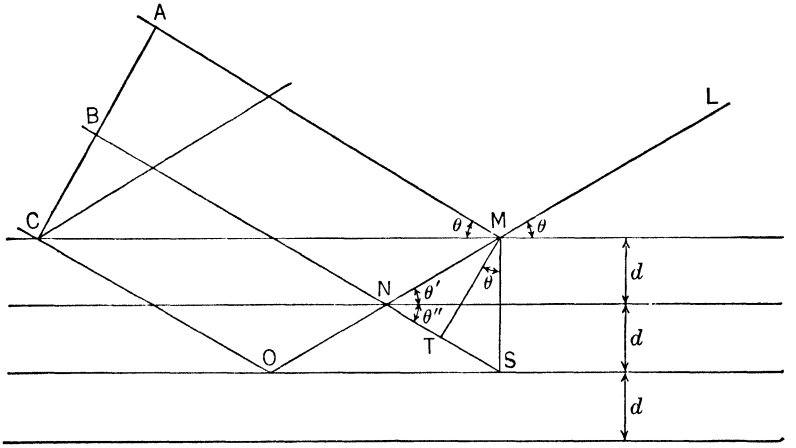


FIG. 32

The path BNL is longer than the path AML by an amount, l, which may be determined by extending BN till it intersects the vertical line MS at S. MT is drawn perpendicular to BS. Then

$$l = NM - NT. \tag{5}$$

NS may be substituted for NM because the angles, θ' and θ'' are both equal to θ, and

$$l = NS - NT = TS. \tag{6}$$

Furthermore,

$$\frac{TS}{MS} = \text{sin angle } TMS = \sin\theta. \tag{7}$$

$$TS = MS \sin\theta. \tag{8}$$

$$MS = 2d. \tag{9}$$

$$l = 2d \sin\theta. \tag{10}$$

When l is one wave-length, λ, or a whole number of wave-lengths 2λ, 3λ or $n\lambda$, the light from the different layers will be reinforced giving maximum intensity, and when it is equal to a fractional number of wave-lengths there will be interference and a weakening of the intensity. Maxima occur when

$$n\lambda = 2d \sin\theta \tag{11}$$

and if X-rays are incident upon the face of a crystal for which d is known, the value of λ for the radiation used may be determined by measuring the angles at which the reflections occur. On the other hand, if the wave-length of the incident radiation is known, it becomes possible to determine the spacing of the atomic planes within the crystal.

In order to study the reflection of X-rays from the faces of crystals, the Braggs devised an instrument known as the X-ray spectrometer, Fig. 33. In this instrument a beam of X-rays passes through a filter at A and is rendered parallel by means of two narrow slits B and B'. After passing through these slits, the rays are reflected from one of the faces of a crystal C, which is mounted as a reflection grating upon the table of the spectrometer, and the reflected beam then passes through a slit D and enters an ionization chamber where its intensity is measured.

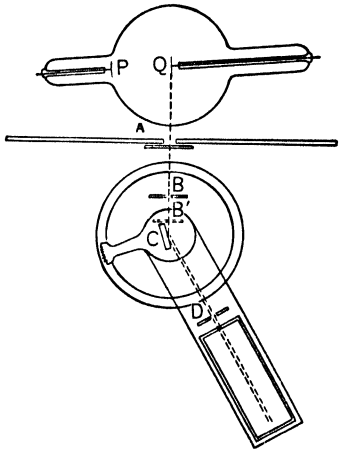


FIG. 33

The ionization chamber contains two electrodes connected to a high-voltage battery through an electrometer. The space between the electrodes is filled with sulphur dioxide or other gas which is easily ionized by X-rays. The magnitude of the electrometer deflection depends on the number of ions formed, which in turn is a measure of the intensity of the X-rays. The crystal and the ionization chamber are rotated about a common axis, the face of the crystal and the ionization chamber being maintained at the same angle as that between the face of the crystal and the incident beam. The intensity of the ionization corresponding to successive settings of the crystal is measured and from these readings the angles corresponding to the maximum reflections are determined.

Crystal Structure of Sodium Chloride. The positions of the maximum reflections from the (100), (110) and (111) faces of a crystal of sodium chloride, obtained with an X-ray tube having a palladium anti-cathode, are shown in Fig. 34. The ordinates represent intensities of ionization as measured by the electrometer. The abscissas represent the degree through which the ionization table is turned starting from a point in line with the slits. These angles must be divided by 2 to obtain the angle, θ, of reflection from the

crystal because the crystal face itself is inclined toward the incident light and the angle of reflection is equal to the angle of incidence. The first order reflections for the planes are found to occur at spectrometer readings of 11.8°, 16.8° and 10.4° for the (100), (110) and

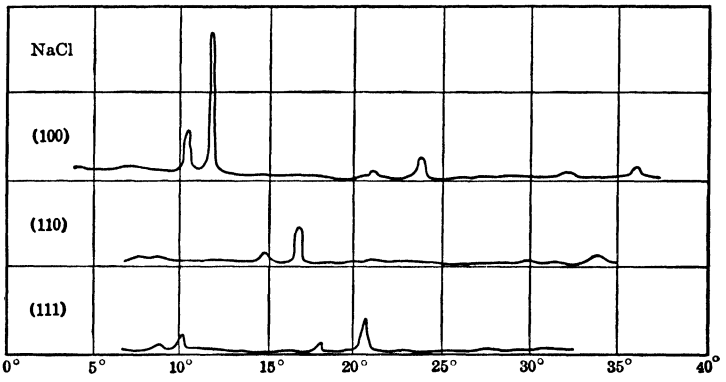


FIG. 34

(111) planes, respectively, corresponding to values of θ of 5.9, 8.4 and 5.2.

Taking the ratio of the sines of these angles, we have

$$\sin 5.9° : \sin 8.4° : \sin 5.2° = 0.103 : 0.146 : 0.091 = 1 : 1.42 : 0.88$$

and since

$$d = \frac{n\lambda}{2 \sin \theta} \tag{12}$$

it follows that the corresponding values of d should be in the ratio of the reciprocals of these numbers, i.e.,

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{1.42} : \frac{1}{0.88} = 1 : 0.704 : 1.14. \tag{13}$$

But we have already seen that for a face-centered cubic crystal

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.155$$

and therefore, the fundamental space-lattice of a crystal of sodium chloride is face-centered.

In this calculation only the first order reflections were used, where $n = 1$. Higher order reflection maxima corresponding to values of n of 2 and 3, etc., are obtained also, but the higher orders become progressively less intense. In the case of the (100) plane in rock salt shown in Fig. 34 there is a first order spectrum at 11.8, a second order

at 23.7 and a third order at approximately 36.3. Taking half of these angles we have $\theta = 5.9°$, $11.85°$ and $18.15°$, and the corresponding sines of these angles are 0.103 : 0.205 : 0.312. The ratios of the sines are very nearly 1 : 2 : 3, as was to be expected.

From any of these angles the interplanar distance, d_{100}, can be calculated. Thus the average value is

$$d_{100} = \frac{n\lambda}{2 \sin \theta} = \frac{1\,\lambda}{2 \times 0.103} = \frac{2\,\lambda}{2 \times 0.205} = \frac{3\,\lambda}{2 \times 0.312} = 4.85\,\lambda. \quad (14)$$

Second order reflection maxima are apparent also in the graph for the (110) plane at 33.6° ($\theta = 16.8$) and for the (111) plane at 20.8° ($\theta = 10.4$).

The crystal lattice may be made up of sodium chloride molecules as units or the parts of the molecule may be separated to give a lattice of sodium atoms or ions, interpenetrating a lattice of chloride atoms or ions. There is a great deal of evidence supporting the view that two separate lattices are involved in sodium chloride and that the sodium ions alternate with chloride ions in the crystal. In this type of crystal the identity of the molecules becomes lost, each sodium atom belonging equally well to six chlorine atoms and each chlorine atom to six sodium atoms. If the term molecule is applied at all, it might be used with reference to the whole crystal. Some types of crystals, however, do have groups of atoms, like molecules, for the units of their crystal lattice.

This sodium chloride lattice is shown in Fig. 35, where the black circles represent chloride ions, and the white circles represent sodium ions. This lattice is strongly supported by the facts shown in Fig. 34. In fact they have not yet been explained in any other way.

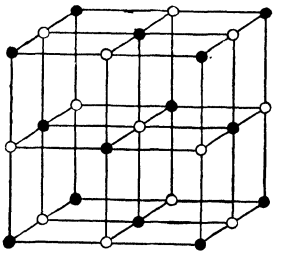


FIG. 35

It will be noted in Fig. 34 that for the (111) plane the first order maximum is very weak, the second order is intense, and the third order is missing. Also from Fig. 35 it will be seen that the (100) and (110) planes contain an equal number of sodium and chlorine atoms, but that in the (111) planes alternate planes contain only sodium atoms, and only chlorine atoms. When X-rays are reflected from the (111) planes, if two chlorine-atom (111) planes are separated by a distance of one wave-length and another plane is set midway between these planes there will be interference because the light is different by exactly half a wave-length. The interference would be complete except for the fact that

the chlorine atoms are 50 per cent heavier* than the sodium atoms and the X-ray reflections from them are more intense. The reflections for the first order spectrum are still present but they are much weakened. For the second order spectrum there is a difference of a whole wave-length between the chlorine and sodium planes and consequently there is no interference. The curve shows that the second order maximum has its full intensity. The third order spectrum again corresponds to a difference of a wave-length and a half, and the interference is effective. This interpretation of the curves through the interpenetrating lattices is further substantiated by the fact that in potassium chloride, which also crystallizes in the same type of lattice, the atoms of chlorine and potassium have approximately the same atomic weight and same number of electrons, and the first and third order maxima are entirely missing in the (111) planes. Potassium bromide, however, with unlike atomic weights gives again a definite but weakened maximum for the first order.

Calculation of Wave-lengths of X-Rays. If the arrangement of the atoms in a crystal of sodium chloride is such as is indicated in Fig. 35, it is a relatively simple matter to compute, not only the interplanar distance d, but also the wave-length of the X-rays employed to establish its crystalline structure.

As will be seen from Fig. 35, in each elementary cubic cell there is one chlorine atom at each corner and also one chlorine atom at the center of each face. Furthermore, since each one of the corner atoms is common to eight similar adjacent cubic cells, only one-eighth of its mass can be considered as belonging to any one of the eight cells. In like manner, each face-centered atom is common to two adjacent cubes and hence contributes only one-half of its mass to each of the two cubes. Therefore, the eight corner atoms contribute the mass of one atom, and the six center atoms contribute the mass of three atoms, to a single cubic cell. In other words, the total mass of chlorine associated with a single cubic cell is equal to the mass of only four chlorine atoms. In precisely the same way, it may be shown that the mass of four sodium atoms is also associated with a single cubic cell, and each cell may be considered as having a mass equal to that of four molecules of sodium chloride. The molar volume of sodium chloride being 27.0 cc., it follows that the volume associated with four molecules, or the volume of a single cubic cell, will be

$$4 \times 27.0/6.06 \times 10^{23} = 178 \times 10^{-24} \text{ cc.}, \qquad (15)$$

* The reflection is determined by the number and distribution of electrons but these in turn are roughly proportional to the atomic weight.

where 6.06×10^{23} is Avogadro's constant, i.e., the actual number of molecules in one gram-molecule of sodium chloride. The length of the edge of the cell is determined by extracting the cube root of 178×10^{-24}, $= 5.62 \times 10^{-8}$ cm. The distance between the planes parallel to the (100) face, d_{100}, will be one-half of this number, or 2.81×10^{-8} cm.

Having determined the value of d_{100} and having previously found that $d_{100} = 4.85\,\lambda$ for X-rays from a palladium anticathode, it follows that

$$\lambda = 2.81 \times 10^{-8}/4.85 = 0.58 \times 10^{-8} \text{ cm.} \qquad (16)$$

It is possible, therefore, to determine the wave-length of X-rays by means of a crystal of known structure in precisely the same manner as in the determination of wave-lengths of light by means of a diffraction grating.

Having determined the wave-length of the X-rays in this manner the interplanar distance in other crystals may be determined by simple application of the formula $n\lambda = 2\,d \sin \theta$.

The Hull, Debye-Scherrer Method of X-Ray Analysis. In the Bragg method already described, a movable ionization chamber was used to determine the position and intensity of the reflection maxima. Sometimes a strip of photographic film is substituted for the ionization chamber but then it is necessary to rotate the crystal by some type of clockwork mechanism so that the planes of the crystal lattice are sure to be set at the proper angle during part of the time to record the maxima in the reflection. Instead of rotating one large crystal, the same results may be achieved by using many small crystals orientated in all directions. This "powder method" was devised almost simultaneously by A. W. Hull* and by Debye and Scherrer.†

If a parallel beam of monochromatic X-rays is allowed to pass through a finely divided crystalline substance, a characteristic spectrum, made up of fine lines, will be produced upon a properly placed photographic film. These lines correspond to the reflections from the different faces of the minute crystalline particles of the powdered substance. Not only does the method of powders furnish essentially the same information as that supplied by the spectrometric method but it does so in a single experiment, whereas, with the spectrometric method, there must be as many separate experiments as there are crystal faces. Furthermore, it has the advantage over the preceding methods that, instead of a well developed crystal of appreciable

* Phys. Rev., **10**, 661 (1917); J. Am. Chem. Soc., **41**, 1168 (1918).

† Physik. Z., **17**, 277 (1916); **18**, 291 (1917).

size, a very small amount of crystalline powder is all that is required; in fact, Hull has found that the amount of material necessary for a complete determination of crystal structure need not be more than one cubic millimeter. In the diagram of Hull's apparatus, shown in Fig. 36, the Coolidge X-ray tube, x is operated by a high voltage transformer; f is a sheet of metal, serving as a filter; S_1 and S_2 are slits in thin sheets of lead; T is a thin-walled tube, about one millimeter in diameter, containing the powdered crystal; F is a narrow strip of photographic film bent over a semicircular strip of brass, concentric with T. A typical spectrogram is reproduced in Fig. 37.

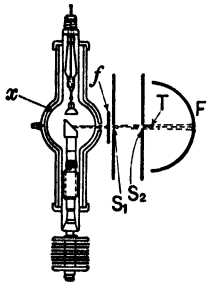


FIG. 36

This method has proved of particular value to the metallographer in determining the crystalline structure of metals and alloys. If, for example, the powder under examination consists of a very large number of minute cubical crystals orientated in all possible directions, some of the crystals will be so placed as to reflect rays from their (100) planes, others from their (110) planes and still others from their (111) planes. But in each case the reflection will take place at a definite angle and will give rise to a series of lines on the

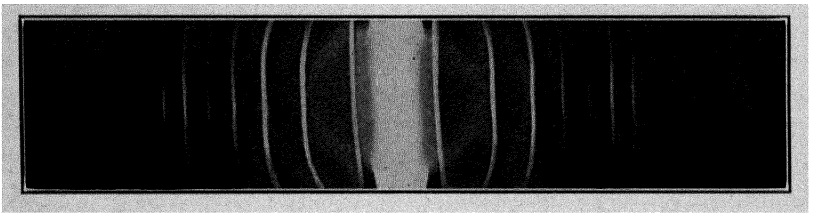


FIG. 37

film corresponding to the reflection maxima for each set of planes. Of course there will be several sets of such lines depending upon the order of reflection. To facilitate the work of the experimenter, a scale is provided which gives directly the spacing — divided by the order of reflection — due to any line on the film when the shadow cast by the powder is placed opposite the zero reading of the scale.

While it is a comparatively easy task to determine the orientation of the atoms in a cubical crystal in which the atoms are all alike, it becomes increasingly difficult to establish the structure of crystals of lower degrees of symmetry and of compounds in which several

kinds of atoms are present. Charts have been devised by Hull and Davey whereby the orientation of the atoms in crystals belonging to the cubic, hexagonal and tetragonal systems may be easily determined. In the case of compounds, it has been found that the heavier atoms containing more electrons reflect the most energy, and, in consequence, the variations in intensity of the lines on the film are significant in the X-ray analysis of compounds.

The powder method has been applied by Hull to the chemical analysis of mixtures of salts. For example, chemical analysis may reveal the presence of sodium, potassium, chlorine and bromine in a given sample and it is necessary to know whether sodium chloride and potassium bromide or potassium chloride and sodium bromide or all four salts are present in the mixture. Although this question cannot be answered by ordinary chemical analysis, Hull has shown that the powder method of X-ray analysis offers an easy solution of the problem. An X-ray photograph of the mixed crystalline powder furnishes a set of lines from which it is possible to determine the composition of the mixture by comparison with similar photographs made with the pure salts alone. Furthermore, by studying the relative intensities of the lines it is even possible to estimate roughly the amounts of each salt present in the mixture.

Miscellaneous Applications of X-Rays. The X-ray analysis of crystals finds many practical applications in different fields. The cubic system has been studied here in some detail because it is the simplest, but the same general methods may be applied to other types of crystals. In the six systems of coördinates there are 230 space groupings and many typical ones have been studied through X-ray measurements.*

In the sodium chloride lattice the crystal units are ions — i.e., atoms which have lost or gained electrons, and they are held together firmly by electrostatic forces. As already pointed out, in such a lattice the molecule loses its identity for there is no special grouping of the atoms except in the whole crystal itself. The force holding such ionic units together is large, and the crystals are hard and mechanically rigid and require a high temperature for fusion. Not all crystals are of this type, however, and in many cases the X-ray analysis shows that several atoms are grouped into units, similar to molecules, which make up the crystal lattice. Naphthalene, solid carbon tetrachloride and solid hydrochloric acid belong to this type

* Wyckoff in " The Structure of Crystals " gives an extensive treatment of this subject.

and, since the units are held together only by weak residual forces, such crystals are soft and have low melting-points.

Crystals which have only a slight degree of symmetry are difficult to interpret and they are difficult to study with X-rays because the crystals are poorly formed and the planes ill-defined. In the examination of organic compounds and crystals containing light elements it is necessary to use soft X-rays produced with a target of copper or other light metal because the X-rays produced by targets of heavy metals are too penetrating.

Similarities in crystal form among different compounds such as that between sodium nitrate and calcium carbonate are readily revealed by X-ray analysis. This test is more reliable than the older test by which one substance was said to be isomorphous (of the same crystalline form) with a second substance if a crystal of the first would grow in a supersaturated solution of the second.

In organic chemistry the long chains and benzene rings which have been used in structural formulas now find experimental support from the data of X-rays. As more CH_2 groups are added to a chain the length of the crystal unit increases approximately 1.3 Å. for each carbon atom but the cross-section remains nearly constant. The hydrocarbon $C_{17}H_{36}$, for example, has a length of 24.3 Å. in the crystal lattice while the hydrocarbon $C_{35}H_{72}$ has a length of 47.7 Å.

X-ray absorption varies with the density of the absorbing solid, and a dense object leaves a shadow on a photographic plate placed behind it. Use of this property is made in the setting of bones, the extraction of teeth, the search for abnormal growths, the location of internal cracks or blow-holes in castings, or the detection of smuggled diamonds.

Many metallurgical operations can now be studied more scientifically through the use of X-rays. Metals have simple crystal lattices and are ductile, whereas the lattices of non-metals are more complex and the material is less ductile. Metals having a face-centered cubic lattice are the most ductile because in this system it is possible to have the greatest interplanar distance — between the (111) planes — and, consequently, the crystal units can slip by each other with the least resistance. Different crystal forms produced by different heat treatments are readily recognized. Iron carbide, for example, when cooled slowly, shows lines which are not present when it is cooled rapidly.

Even material which is not ordinarily classed as crystalline may be tested with X-rays, as for example, fibers, rubber, shellac, cellulose compounds, and asbestos. A photograph through a pin-hole with

monochromatic X-rays gives concentric rings for powders and symmetrical arcs for fibers.

Heat Capacity of Solids. Many investigations of specific heats of solids at extremely low temperatures have resulted in the formulation of several interesting relationships between heat capacity and temperature.

At ordinary temperatures the molecules or atoms of a crystal may be assumed to be in a state of violent motion. As the temperature is lowered the amplitude of the various oscillations steadily diminishes, until finally at the absolute zero, there is in all probability a complete cessation of motion. Near the absolute zero, where the amplitude of the atomic oscillations is negligible, a crystalline solid may be assumed to possess the properties characteristic of a perfectly elastic body. In other words, the crystalline forces holding the units together would preponderate over the feeble thermal forces tending to initiate atomic oscillations within the solid. Under these conditions the solid as a whole would exhibit the same behavior as a single molecule, that is to say, the solid would function as a perfectly elastic body.

On this assumption Debye* has derived the following equation expressing the heat capacity of a solid, C_v, in terms of its absolute temperature, T,

$$C_v = 71.9 \frac{T^3}{\theta^3}. \tag{17}$$

In this equation θ is a constant characteristic of each solid and has the same dimensions as T. The value of θ varies between the limits $\theta = 50$ for calcium and $\theta = 1840$ for carbon. The agreement between the observed and calculated values of C_v has been found to be excellent up to $T = \theta/12$.

When this latter temperature is exceeded, the units of the solid begin to absorb more and more heat energy and to vibrate independently about their centers of oscillation. The failure of Debye's equation is to be expected under these conditions since the solid is no longer behaving as one large molecule. Obviously the lighter the atoms and the greater the crystalline forces within the solid, the higher must the temperature become before the individual atoms can acquire appreciable kinetic energy. This is apparent from the familiar dynamical principle, that the kinetic energy of a vibrating particle is proportional to its mass and to the square of its vibration frequency. In the case of

* Ann. Physik, **39**, 789 (1912).

lead, which is a soft, malleable solid with a relatively low melting-point, it is reasonable to infer that the crystalline forces are feeble, and consequently we should expect that molecular and atomic vibrations would be set up at quite low temperatures. Furthermore, since the atoms of lead are extremely heavy, their kinetic energy must be great. The correctness of these conclusions is confirmed by the fact that the Debye equation when applied to lead has been found to hold only over a very short range of temperature. On the other hand, the equation has been found to hold for the diamond up to a temperature

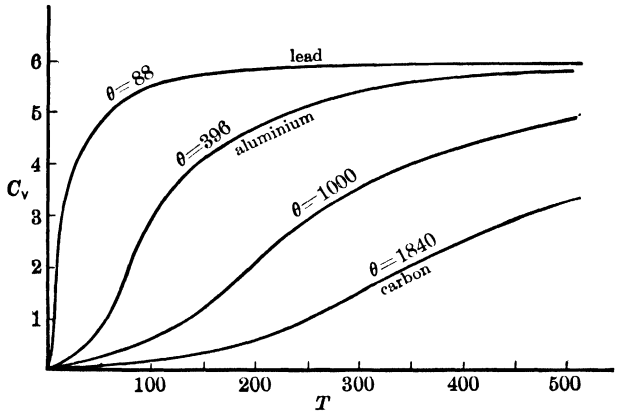


FIG. 38

of about 200° absolute. In this case we have a solid in which the crystalline forces are extremely powerful and in which the atoms are relatively light. A fairly high temperature must be attained before the energy absorbed by the individual atoms of the diamond acquires appreciable magnitude.

The absorption of energy by the vibrating units continues to increase as the temperature is raised until ultimately, at the melting-point of the solid, the crystalline forces become negligible. As this temperature is approached, therefore, the intermolecular restraint becomes less and less and the mean kinetic energy of the molecules approaches that of the molecules of the molten solid.

At room temperatures most of the solid elements, except those of low atomic weight, have reached a temperature at which they have the limiting value of atomic heats, as shown in Fig. 38. In 1819 Dulong and Petit discovered the interesting fact that *the product of the specific heat and the atomic weight of the solid elements is a constant, approximately* 6.4. This law of Dulong and Petit played an im-

portant part in the determination of atomic weights, for it served to show from a simple specific heat measurement what multiple of the combining weight should be taken for the atomic weight in order to obtain the constant 6.4. Lewis* has directed attention to the fact that it is much more rational to calculate the atomic heat of an element from the specific heat at constant volume rather than from the specific heat at constant pressure. In the latter case there are secondary effects depending on the thermal expansion and compressibility which tend to mask the more fundamental relation. Although it is difficult to measure the specific heats at constant volume their values may be derived from the specific heat at constant pressure by an application of the laws of thermodynamics as follows:

$$C_p - C_v = \frac{T\alpha^2 V}{41.3\,\beta}, \tag{18}$$

where T is the absolute temperature, α the volume coefficient of thermal expansion, β the coefficient of compressibility, C_p and C_v the atomic heat capacity (specific heat multiplied by atomic weight) at constant pressure and constant volume, and V the atomic volume. Lewis and Gibson† found that the atomic heat capacity at constant volume and room temperature is 5.9 within 0.09 for all the elements heavier than potassium for which data were available.

It will be noted that this value of 5.9 for the atomic heat capacity of a crystal is nearly three times the gas constant. Moreover, it will be remembered that the heat capacity of a monatomic gas at constant volume is $3/2\,R$. There is a theoretical reason why the atomic heat capacity of a crystal should be twice that of a monatomic gas. In the latter case heat is absorbed only in giving the molecule increased kinetic energy, but in a crystal the units of the lattice have definite positions and when they are displaced they acquire potential energy which is equal to the kinetic energy required to displace them. Twice as much heat energy then is necessary to raise the temperature 1°.

In the case of a solid having a high melting-point, the violent agitation of its constituent molecules and atoms, as the temperature is raised, will undoubtedly produce a corresponding increase in the amplitude of vibration of its electrons together with an increase in their translational velocity among the molecules. Under these conditions, the specific heat at constant volume should be greater than 5.9 calories. This conclusion cannot be verified experimentally until

* J. Am. Chem. Soc., **29**, 1165 (1907).

† J. Am. Chem. Soc., **39**, 2554 (1917).

the values of α and β in the foregoing equation have been determined at high temperatures.

The complete heat capacity curves for three typical solid elements, lead, aluminum, and carbon, are given in Fig. 38. It is apparent from these curves that the absorption of heat energy by a crystalline solid may be considered as taking place in three distinct stages, as follows: — (1) In the neighborhood of the absolute zero, the heat capacity remains practically zero; (2) the heat capacity increases rapidly with the temperature; and (3) the heat capacity increases slowly, approaching asymptotically the limiting value 5.9 for $T = \infty$. For a malleable, low-melting element of high atomic weight, such as lead, the first two stages are very short and the final stage commences at a low temperature. On the contrary, with a hard, high-melting element of low atomic weight, such as carbon in the form of diamond, the final stage is not reached at any temperature within the range covered by the experiments.

Liquid Crystals. In addition to possessing well-defined geometrical forms, crystalline substances are characterized by their resistance to deformation when subjected to mechanical stress, and by the property of melting sharply at definite temperatures with the production of transparent liquids.

In 1888, two substances, cholesteryl acetate and cholesteryl benzoate, were found by Reinitzer* to behave in an anomalous manner when heated. At definite temperatures these substances melted to turbid liquids which, in turn, became clear on further heating, the latter change also taking place at definite temperatures. On cooling the clear liquids, the reverse series of changes was found to occur.

Examination of the turbid liquids revealed the fact that they resembled ordinary liquids in their general behavior, such as assuming the spherical shape when suspended in a medium of the same density, or of rising in a capillary tube under the influence of surface tension. But in addition to possessing the properties characteristic of the liquid state, Lehmann discovered that they possessed optical properties which had hitherto been observed only with solid, crystalline substances. Their behavior towards polarized light was such as to warrant the conclusion that these turbid liquids are anisotropic. In view of these facts, Lehmann proposed that liquids possessing these properties should be called *liquid crystals*, the term implying that, under ordinary conditions, the crystalline forces in these substances are so feeble that the crystals readily undergo deformation and actually flow like liquids. That these turbid liquids

* Monatshefte, **9**, 435 (1888).

are not emulsions is proved by the fact that when they are examined under the microscope, the turbidity is found to be due to the aggregation of a myriad of differently oriented transparent crystals. All subsequent investigation of liquid crystals has failed to show any lack of homogeneity. The number of such substances known at the present time is fairly large.

REFERENCES

An Introduction to Crystal Analysis. Bragg.
The Structure of Crystals. Wyckoff.
Applied X-Rays. Clark.
Flüssige Krystalle. Lehmann.
Crystalline Form and Chemical Constitution. Tutton.
X-Rays in the Service of Chemistry and Industry in 1931. Clark, J. Chem. Education, **8**, 625 (1931).

PROBLEMS

1. A certain crystal face intercepts the X axis at $4\,a$, the Y axis at b and the Z axis at $\frac{1}{8}\,c$. What are its Miller indices?

2. MnO has the NaCl-type cubic lattice and the edge of the unit cube is 4.40 A. The unit contains the equivalent of 4 ions of each kind. What is the density of the crystal? *Ans.* 5.50.

3. Caesium bromide crystallizes as a body centered cubic crystal. In the Bragg spectrometer using X-rays of 0.576 Å a first order maximum for the (100) plane was obtained at an angle of θ of 7° 43′. What is the interplanar distance d_{100}? The length of the unit cell is $2 \times d_{100}$ and it contains the equivalent of one molecule of CsBr. What is the density of the caesium bromide?

4. In the reflection of X-rays of wave-length 0.576 Å by a certain crystal, first order maxima for the (100), (110) and (111) planes are obtained when θ is 6° 54′, 9° 52′ and 6° 00′ respectively. What are the values of d_{100}, d_{110}, and d_{111} and what type of lattice has this crystal?

5. At 20° the molar heat capacity C_p of sodium is 6.90, the density is 0.97, the volume coefficient of thermal expansion α is 0.00021 and the coefficient of compressibility β is 0.000016. What is the molar heat capacity at constant volume C_v of sodium at 20°? *Ans.* 6.44 cal. per degree.

6. Calculate the molar heat capacity at constant volume C_v of lead at 20°. The density is 11.34. The molar heat capacity at constant pressure, C_p, is 6.3. The volume coefficient of thermal expansion α is 0.000087 and the coefficient of compressibility β is 0.0000022.

CHAPTER V

THE RELATION BETWEEN PHYSICAL PROPERTIES AND MOLECULAR CONSTITUTION

Before proceeding to a brief consideration of several examples illustrating the dependence of physical properties upon molecular constitution, it should be pointed out that there are two different ways in which such relationships may be approached. Thus, we may seek to determine the influence which the number and kind of the atoms present in different molecules exert upon some particular physical property; or, on the other hand, we may strive to ascertain how the property in question is influenced by the manner in which the atoms are arranged in the molecule. The first method serves to bring out the *additive* character of the property, whilst the second method emphasizes its *constitutive* character. Almost all physical properties exhibit both additive and constitutive characteristics. In addition to additive and constitutive properties, Ostwald has introduced a third type which he calls *colligative* properties; the numerical value of a colligative property is entirely dependent upon the *number* of molecules present. For example, the volume of a gas is a colligative property since it is practically proportional to the total number of molecules present in the gas. Obviously, since colligative properties are independent of both composition and structure, they call for no further consideration in this chapter.

Molar Volume. In dealing with the volume relations of liquids it is customary to employ the *molar volume*, i.e., the volume occupied by the molecular weight of the liquid in grams. The justification for this procedure is that, when we compare the gram-molecular weights of liquids, the comparison involves equal numbers of molecules of the different substances.

Relations between the molar volumes of liquids were first pointed out by Kopp.* On comparing the molar volumes of different liquids at their boiling-points, he found that constant differences in composition correspond to approximately constant differences in the molar volumes. Thus, the molar volumes of the successive members of an homologous series differ by the same number of units, this

* Lieb. Ann., **41**, 79 (1842); **96**, 153, 303 (1855).

difference corresponding, for example, to a CH_2 group. In like manner, the molar volumes of various groups have been determined, and from these in turn the atomic volumes of the constituent elements have been worked out.

While Kopp found that his results were most regular when the molar volumes were determined at the boiling temperatures of the respective liquids, the reason for this did not appear until after van der Waals had developed his theory of corresponding states. As has already been pointed out, the boiling-points of most liquids are approximately two-thirds of their respective critical temperatures, and therefore the liquids are in corresponding states.

The following values of the atomic volumes are those recently published by Le Bas* and represent the average values derived from the study of a large number of organic compounds of widely different character:

C = 14.8	Cl = 22.2	I = 37.0	N = 15.6	
H = 3.7	Br = 27.0	S = 25.6	= 10.5	(in primary amines)
O″ = 7.4 (as in aldehydes, ketones and doubly linked oxygen generally)			= 12.0	(in secondary amines)
O′ = 9.1 (in methyl esters)				
= 11.0 (in higher esters)		>O = 9.9 (in methyl ethers)		
= 12.0 (in acids)		= 11.0 (in higher ethers)		

As will be seen, the value of the atomic volume is partly dependent upon the manner of linkage of the atoms in the molecule.

By means of such a table of experimentally determined atomic volumes it is possible to calculate the molar volumes of the lower members of the various homologous series of organic liquids with a fair degree of accuracy. For example, the molar volume of acetic acid, $C_2H_4O_2$, may be calculated from the atomic volumes of its constituent atoms as follows: —

2 C	$= 2 \times 14.8 = 29.6$
4 H	$= 4 \times 3.7 = 14.8$
1 O′	$= 1 \times 12.0 = 12.0$
1 O″	$= 1 \times 7.4 = 7.4$
	Molar volume 63.8

The density of acetic acid at its boiling-point is 0.942 and its molec-

* The Molecular Volumes of Liquid Chemical Compounds.

ular weight is 60, therefore the observed value of the molar volume is, 60/0.942 = 63.7, a result which is in excellent agreement with that calculated from the atomic volumes of the constituent atoms. The following table gives the calculated and observed values of the molar volumes of a number of different organic compounds at their boiling-points: —

MOLAR VOLUMES

(Cubic centimeters per mol)

Substance	Formula	V_m(calc.)	V_m(obs.)
Methyl alcohol	CH_4O	38.7	42 0
Ethyl alcohol	C_2H_6O	60.9	62.0
Amyl alcohol	$C_5H_{12}O$	127.5	124.0
Acetaldehyde	C_2H_4O	51.8	56.5
Acetone	C_3H_6O	74.0	77.5
Formic acid	CH_2O_2	41 6	41.3
Acetic acid	$C_2H_4O_2$	63.8	63.7
Propionic acid	$C_3H_6O_2$	86 0	85.4
Methyl formate	$C_2H_4O_2$	60.9	63.4
Methyl acetate	$C_3H_6O_2$	83.1	85.8
Ethyl ether	$C_4H_{10}O$	107 2	106 0
Benzene	C_6H_6	111.0	96.0
Naphthalene	$C_{10}H_8$	177.6	149 2

It is apparent from the data of the foregoing table that although the agreement between the observed and calculated values of the molar volumes is in some cases very satisfactory, in other cases the differences are so great as to engender doubt as to the reliability of this simple generalization. The agreement in the case of acetic acid is somewhat better than usual. The relation breaks down completely in the case of inorganic or highly polar liquids where the attractive force between molecules is so great as to cover up the additive properties of the atomic volumes. Ring structure, as in the case of benzene, produces a large shrinkage in the molar volume: 2.45 cc. for each carbon atom in the ring. In spite of its limitations, Kopp's relation is sometimes useful in distinguishing between different structural formulas for an organic compound, that structure being chosen which causes the sum of the atomic volumes to agree with the experimentally determined molar volume. It can be used also for practical approximations in estimating the molar volumes of liquids or their densities at the boiling-point.

Sugden's parachor* constitutes a refinement of the application of molar volumes to the problem of molecular constitution. The term parachor signifies comparative volume. It is designated by P and defined by the equation

$$P = \frac{m}{D - d}\gamma^{\frac{1}{4}}, \tag{1}$$

where m is the molecular weight, D is the density of the liquid, d is the density of the saturated vapor and γ is the surface tension, all measured at the same temperature. The density d of the vapor is measured at a pressure equal to the vapor pressure. It is negligible when the vapor pressure is low. The equation is based on a relation due to Macleod according to which the surface tension of an unassociated liquid is proportional to the fourth power of the difference between the densities of the liquid and vapor. Roughly speaking, a comparison of P for different substances gives a comparison of molar volumes at temperatures at which the liquids have the same surface tension.

Since surface tensions are connected with the internal pressures of the liquids, Sugden believes that a comparison at equal surface tensions is more likely to bring out regularities in organic compounds than a comparison at equal vapor pressures, i.e., at the boiling-points. The value of P is 4.8 for carbon, 17.1 for hydrogen, 20 for oxygen, 54.3 for chlorine, 23.2 for a double bond, 6.1 for a six-membered ring, etc. Although Sugden's relation must be regarded as empirical the calculated and observed values of the parachor agree remarkably well (within one per cent) for a large number of organic compounds. The parachor has been used to study structure with reference to the newer theories of valence and has been helpful in connection with newly discovered types of isomers.†

Refractive Index of Liquids. The velocity of transmission of light through any medium depends upon its nature, especially upon its density. When a ray of light passes from one medium into another it is refracted, the amount of refraction being such that the ratio of the sines of the angles of incidence and refraction is constant and characteristic for the two media. This fundamental law of refraction was discovered by Snell about 1621. According to the wave theory of light, the ratio of the sines of the angles of incidence and refraction is identical with the ratio of the velocities of light in the two media. The ratio is termed the *index of refraction* and is usually denoted by

* Sugden, J. Chem. Soc., **125**, 1177 (1924).

† Fuson, Chem. Rev., **7**, 360 (1930).

the letter n. Representing by i and r the angles of incidence and refraction, and by v_1 and v_2 the respective velocities of light in the two media, we have

$$n = \frac{\sin i}{\sin r} = \frac{v_1}{v_2}. \tag{2}$$

Various forms of apparatus have been devised for the determination of the refractive index of liquids. Of these a well known and accurate one is the refractometer of Pulfrich, the principles of which may be understood with the help of Fig. 39. The liquid or fused solid is placed in a small glass cell C, which is cemented to a rectangular prism P of dense optical glass, the refractive index of which is generally about 1.61. A beam of monochromatic light, from a sodium flame or a spectrum-tube containing hydrogen, is allowed to enter the prism in a direction parallel to the horizontal surface of separation between the glass and the liquid. After passing through the liquid and the prism, the beam emerges making an angle i with its original direction. By means of a telescope, the emergent beam can be observed and its position noted, the angle of emergence being read on a divided circle attached to the telescope. From the angle of emergence thus determined, the index of refraction of the liquid can be calculated in the following manner. The value of the index of refraction, N, for air/glass being known, we have

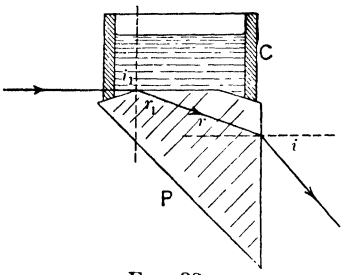


FIG. 39

$$N = \frac{\sin i}{\sin r}. \tag{3}$$

The angle of incidence of the last ray entering the prism from the liquid is 90°, or $\sin i_1 = 1$. The index of refraction, n_1, for liquid/glass may be calculated thus,

$$n_1 = \frac{\sin i_1}{\sin r_1} = \frac{1}{\sin r_1}. \tag{4}$$

But

$$\sin r_1 = \cos r = \sqrt{1 - \sin^2 r}. \tag{5}$$

Transposing equation (3) and substituting in equation (5), we have

$$\sin r_1 = \sqrt{1 - \frac{\sin^2 i}{N^2}},$$

or

$$\sin r_1 = \frac{1}{N}\sqrt{N^2 - \sin^2 i}. \tag{6}$$

Therefore, substituting equation (6) in equation (4), we have

$$n_1 = \frac{N}{\sqrt{N^2 - \sin^2 i}}. \tag{7}$$

The index of refraction, n, for air/liquid is equal to N/n_1 and by substitution in equation (7),

$$n = \sqrt{N^2 - \sin^2 i}, \tag{8}$$

or if $N = 1.61$,

$$n = \sqrt{2.5921 - \sin^2 i}. \tag{9}$$

The values of $\sqrt{N^2 - \sin^2 i}$ are generally given, for different values of i, in tables supplied with the refractometer, thus saving the experimenter a somewhat laborious calculation. The value of n thus obtained is the index of refraction from air into the liquid; if the index from vacuum into the liquid, the so-called *absolute index*, is required, the value of n must be multiplied by 1.00029.

The index of refraction is dependent upon the wave-length of the light employed, the index for the red rays being less than that for the violet rays. It is therefore necessary in making measurements of refractive indices to use light of a definite wave-length, or what is termed *monochromatic light*. The sodium flame is most frequently used for this purpose, the wave-length being represented by the letter *D*. Measurements of the refractive index referred to the *D*-line of sodium are commonly designated by the symbol n_D. When incandescent hydrogen is employed as a source of light, the refractive index may be determined for the *C*-, *F*- and *G*-lines, the respective values being represented by n_C, n_F, and n_G.

In certain other types of refractometers white light containing many different wave-lengths is used, and a compensating prism is adjusted for each liquid so as to eliminate the color fringe. The refractive index of a substance may be measured with accuracy; it is used in checking the purity of a substance the refractive index of which is known, and in determining the composition of a solution from a knowledge of the refractive index of solutions of known composition.

Specific and Molar Refractions. The refractive index, n, of a liquid varies with temperature and pressure as the number of molecules in the path of the light is changed, but the specific refraction

is quite independent of these variables. On the basis of the electromagnetic theory of light, Lorenz and Lorentz* have shown that

$$r = \frac{1}{d}\frac{n^2 - 1}{n^2 + 2}, \tag{10}$$

where r is the specific refraction, n is the refractive index and d the density.

In order that we may compare the refractive powers of different liquids, the specific refractions are multiplied by their respective molecular weights, the resulting products being termed their *molecular refractions*. As the result of a large number of experiments, it has been shown that the molecular refraction of a compound is made up of the sum of the refractive constants of the constituent parts, or in other words refractive power is an additive property. The values of the refractive constants of the elements and commonly occurring groups have been determined with great care by Brühl and others, the method employed being similar to that used by Kopp in connection with his investigations on molecular volumes. Thus, Brühl found in the homologous series of aliphatic compounds that a difference of CH_2 in composition corresponds to a constant difference of 4.57 in molecular refraction. Then, having determined the molecular refraction of a ketone or an aldehyde of the composition, $C_nH_{2n}O$, he subtracted n times the value of CH_2 and obtained the atomic refraction of carbonyl oxygen. By subtracting the molecular refraction of the hydrocarbon, C_nH_{2n+2}, from that of the corresponding alcohol, $C_nH_{2n+2}O$, he obtained the atomic refraction of hydroxyl oxygen. By subtracting six times the value of CH_2 from the molecular refraction of hexane, C_6H_{14}, he obtained the refractive constant for hydrogen or 2 H = 2.08. In like manner the refractions of other elements and groups of elements were determined.

Just as in the case of molecular volumes so with molecular refractions, the measurements may be used to decide questions of molecular structure. Brühl,† who devoted much time to the investigation of the effect of constitution upon refraction, pointed out that the molecular refraction of compounds containing double and triple bonds is greater than the calculated value, and he assigned to these bonds definite constants of refraction. The values of the atomic refractions for a few of the elements are given in the following table.‡

* Wied. Ann., **9**, 641 (1880).

† Proc. Roy. Inst., **18**, 122 (1906).

‡ In this connection a paper entitled " Atomic Refraction " by W. Swietoslawski, J. Am. Chem. Soc., **42**, 1945 (1920), is recommended.

ATOMIC REFRACTIONS

Element or Structural Feature	Mr_D
Carbon singly bound and occurring alone, C*	2.592
Carbon singly bound, C′	2.501
Hydrogen, H	1.051
Hydroxyl oxygen, O′	1.521
Ethereal oxygen, O <	1.683
Ketonic oxygen, O″	2.287
Double bond, =	1.707
Triple bond, ≡	2.10
Chlorine, Cl	5.998
Bromine, Br	8.927
Iodine, I	14.12

When applied to simple compounds of carbon, hydrogen and oxygen the agreement between the observed and calculated values of molecular refractions is generally very satisfactory. For example, we may compare the calculated and observed values of the molecular refraction of lactic acid, employing the Lorenz-Lorentz formula. The formula of lactic acid is, $CH_3CHOHCOOH$, or $C_3H_6O_2'O''$, hence the molecular refraction is calculated as follows: —

$$\begin{aligned} 3\,C &= 3 \times 2.501 = 7.503 \\ 6\,H &= 6 \times 1.051 = 6.306 \\ 2\,O' &= 2 \times 1.521 = 3.042 \\ 1\,O'' &= 1 \times 2.287 = 2.287 \\ \text{Molecular refraction} &= 19.138 \end{aligned}$$

The observed value of the molecular refraction of lactic acid is 19.138.

It has been found that the refractive power of a substance is influenced not only by the presence of double and triple bonds, but also by the relative position of such bonds within the molecule. When a molecule contains only one double or triple bond, the molecular refraction may still be calculated with considerable accuracy from the values of the atomic refractions, due allowance being made for the condition of unsaturation. When, however, a second double or triple bond is introduced into the molecule in a position adjacent to the first, the calculated value of the molecular refraction is found to differ appreciably from the observed value. This phenomenon is known as *optical anomaly.*

The determination of the molecular refraction of a liquid affords a means of ascertaining or confirming its chemical constitution. For example, geraniol has the formula $C_{10}H_{18}O$, and its chemical behavior is such as to warrant the conclusion that it is a primary alcohol. The value of n_D is 1.4745, from which the molecular refraction is calculated

to be 48.71. The molecular refraction calculated from the atomic refractions given in the preceding table is: —

$$\begin{aligned} 10\ \text{C} &= 10 \times 2.501 = 25.01 \\ 18\ \text{H} &= 18 \times 1.051 = 18.92 \\ 1\ \text{Hydroxyl O} &= 1 \times 1.521 = 1.52 \\ \text{Molecular refraction} & \qquad\qquad 45.45 \end{aligned}$$

The difference between the theoretical and experimental values of the molecular refraction is 48.71 − 45.45 = 3.26, which is approximately twice the value of a double bond, 1.707 × 2 = 3.414. From this we conclude that the molecule of geraniol contains two double bonds. Furthermore an alcohol of the formula, $C_{10}H_{18}O$, containing two double bonds cannot possess a ring structure and therefore must be a member of the aliphatic group of compounds. This conclusion is supported by the chemical properties of the substance. The accepted structural formula of geraniol is

$$(CH_3)_2C = CH\cdot CH_2\cdot CH_2 - \overset{\displaystyle H - C - CH_2OH}{\overset{\displaystyle \|}{C}} - CH_3.$$

In a similar manner the Kekulé formula for benzene has been confirmed, the difference between the theoretical and experimental values of the molecular refraction indicating the presence of three double bonds in the molecule.

Thus, Brühl* found that on changing from an acetylene to an ethylene linkage there is a decrease of 0.40 units in molecular refractive power, and also that in the polymerization of acetylene to benzene, as represented by the equation,

$$3\ C_2H_2 = C_6H_6,$$

a decrease of 1.19 units in refractive power occurs. Since the decrease in refractive power is approximately three times the change in refractive power resulting from the replacement of a triple by a double bond, Brühl inferred that in a molecule of benzene there must be three double bonds as in the familiar formula proposed by Kekulé.

Rotation of the Plane of Polarized Light. Some liquids, when placed in the path of a beam of polarized light, possess the property of rotating the plane of polarization to the right or left. Such liquids are said to be optically active. The determination of the rotatory power of a substance is made by means of a polarimeter, the essential parts of which are two similar Nicol prisms placed one behind the other

* Z. physik. Chem., **1**, 343 (1887).

with their axes in the same straight line as shown in Fig. 40. The light after passing through the forward prism P, known as the *polarizer*, has its vibrations reduced to a single plane; it is said to be plane polarized. On entering the rear Nicol prism A, known as the *analyzer*, the light will either pass through or be partially or completely stopped, depending upon the position of the prism. If the analyzer is rotated, so that its axis is at right angles to the axis of the polarizer, the field observed will be dark, no light being transmitted. If now a tube similar to that shown in Fig. 40 is filled with an optically active liquid and placed between the polarizer and analyzer, the field will become light again, owing to the rotation of the plane of polarization by the opti-

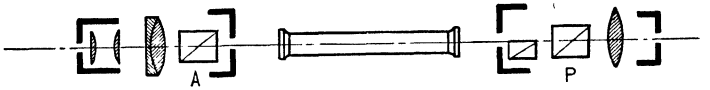


FIG. 40

cally active substance. The extent to which the plane of polarization has been rotated can be determined by turning the analyzer until the field becomes dark again, and reading on a graduated circle, the number of degrees through which it has been moved. When it is necessary to turn the analyzer to the right, the substance is dextro-rotatory, and when it is necessary to turn it to the left, the substance is levo-rotatory.

A half shadow field with the light polarized in the two halves at slightly different angles aids in the accuracy of the reading, for the analyzer can be so turned that the two fields just match and the line of separation disappears.*

Specific and Molar Rotation. The extent of the optical rotation depends on several factors, including the nature of the liquid, the length of the column through which the light passes, the wave-length of light used and the temperature. It becomes necessary then to define the specific rotation as follows:

$$[\alpha]_t^{\lambda} = \frac{\alpha}{ld} \qquad (11)$$

where $[\alpha]_t^{\lambda}$ is the specific rotation, α is the observed angle, l the length in decimeters, and d the density; t refers to the temperature and λ to the wave-length of light used. The yellow light of sodium, the D line, is usually used and it may be assumed unless otherwise specified. The green line of the mercury arc is also used. The molar rotation $[\alpha_M]$

* Further details are given in "The Optical Rotatory Power of Organic Substances and its Practical Applications," Landolt, translated by Long.

is obtained by multiplying the specific rotation by the molecular weight, and often one-hundredth of this value is taken as the unit.

The specific and molar rotations of solutions of optically active substances may be determined also, if we assume that the solvent is without effect. While this assumption is apparently satisfactory with aqueous solutions, it is unsatisfactory when non-aqueous solvents are used. The optical rotation depends not only on the length of the solution but also on the concentration, and if g grams of an optically active substance are dissolved in v cc. of solution, then

$$[\alpha]_t^\lambda = \frac{\alpha}{lg/v} = \frac{\alpha v}{lg} \tag{12}$$

and if g grams are dissolved in w grams of solution, the density of the solution being d, then, since $v = w/d$

$$[\alpha]_t^\lambda = \frac{\alpha w}{lgd}. \tag{13}$$

Optical Activity and Chemical Constitution. Optical activity is most often found in compounds containing an asymmetric carbon atom, that is, a carbon atom which is attached by its valence bonds to four different atoms or groups of atoms. This is a matter of great importance in organic chemistry and has in fact laid the foundation of stereochemistry. One of the simplest examples of optically active compounds is lactic acid, which has the structural formula

$$\begin{array}{c} H \\ | \\ CH_3 - C - COOH \\ | \\ OH \end{array}$$

If the four valencies of the tetrahedral carbon atom are satisfied with different atoms or groups, no plane of symmetry can be passed through

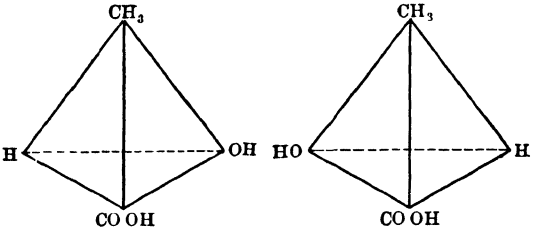


FIG. 41

the figure. Two different optical isomers are then possible, dextro- and levo-lactic acid, as shown in Fig. 41.

They are practically identical in their properties except that they rotate the plane of polarized light in opposite directions. When lactic acid, or other material containing an asymmetric carbon atom, is synthesized in the laboratory a mixture containing equal parts of each form is produced. Such a mixture is called a racemic mixture, and it may be separated into its optical isomers by forming derivatives with optically active bases, usually alkaloids, which have different solubilities. In a second method one or the other isomer is destroyed by micro-organisms. For example, if the bacterium *penicillium glaucum* is introduced into a solution of racemic tartaric acid, it will thrive at the expense of the dextro acid and leave the pure levo form. In a third method the two different isomers are allowed to crystallize in different forms which are then separated by hand picking.

The magnitude of the rotation is in part connected with the relative masses of the atoms or groups of atoms surrounding the central asymmetric carbon atom, and some regularities occur in homologous series, but no completely satisfactory generalizations have been made. In some cases the specific rotation of a solute is the same in different solvents, but usually it varies in a manner which is specific for each solvent and solute. Apparently some loose combination with the solvent at certain parts of the molecule changes the rotation in a manner which cannot now be predicted. Ionization of the optically active molecule usually leads to a marked change in the specific rotation. Optical activity is not restricted to the asymmetric carbon atom, and it has been observed in the case of compounds containing asymmetric atoms of nitrogen, sulphur, tin, cobalt, and others. Moreover it has been observed in certain types of organic compounds which contain an unsymmetrical grouping but no asymmetric carbon atom.

Crystals sometimes exhibit optical rotation which may be explained in two different ways. Quartz, for example, rotates the plane of polarized light by virtue of the spiral arrangement of units in the crystal lattice whereas certain other types of crystals rotate the light because the molecules themselves are optically active. The proof that crystals of tartaric acid with "right-handed faces" give a solution which is dextro-rotatory and that "left-handed faces" give solutions which are levo-rotatory constituted one of the brilliant researches of Louis Pasteur.* In this case the rotation is due to the molecules as well as to the arrangement in the crystal.

Magnetic Rotation. Many substances acquire the power of rotating the plane of polarized light when placed in an intense magnetic field. This fact was first discovered by Faraday in 1846, and the

* Ann. chim. phys., **24**, 442 (1848); **31**, 67 (1851).

phenomenon has been studied extensively by Perkin.* A tube of a liquid is placed axially between the perforated poles of a powerful electromagnet, and the plane of polarization of light from a sodium flame or other source is rotated to the right or left, depending on the direction of the current. The molecular magnetic rotation for many organic compounds is an additive property but the structure of the molecule exerts a great influence. Consequently, the regularities which have been discovered for molecular refraction and molar volume are only approximately satisfied by magnetic rotation.

Absorption of Light. When a ray of light traverses any transparent or translucent medium, a portion of the radiant energy is absorbed and the emergent ray does not contain the vibrations which have been taken up. The spectrum of the emergent light is characterized by dark bands corresponding to the wave-lengths of the incident light which have been absorbed. Such a spectrum is known as an *absorption spectrum*, and is characteristic for each individual substance under specified conditions. The phenomenon of absorption is exhibited by gases, liquids and solids. In the case of some solids and liquids, however, the opacity is so great that incident radiation can penetrate only a short distance below the surface. The characteristic absorption of a solid may be determined, nevertheless, by observing the spectrum of the light reflected from its surface.

Two distinct types of absorption are recognized, namely, *general* and *selective* absorption. In the former, the intensity of the transmitted light is diminished equally throughout large regions of the spectrum, whereas in the latter there are marked inequalities in the intensity of the transmitted light, resulting in the formation of bands of varying width in different parts of the spectrum. It often happens that both general and selective absorption occur together in the same spectral region and, when this is the case, the selective absorption is apt to be masked by the general absorption. Owing to the greater persistence of selective absorption, however, the effect of general absorption may be practically eliminated by diluting the substance with a non-absorbing solvent and thus lessening the number of absorbing units in the path of the incident light.

The mechanism by which the light is absorbed will be discussed in Chapters XX and XXIV, but it may be stated here that absorption bands in the visible and ultra-violet regions are due to the displacement of the valence electrons in molecules. Absorption in the infra-red region where the wave-lengths are longer is due to the displacement of atoms.

* J. Chem. Soc., **69**, 1025 (1896).

Measurement of Absorption. Absorption in the ultra violet is measured with the photographic plate; absorption in the visible is readily detected either with the eye or with a photographic plate. Infra-red radiation affects neither the eye nor the ordinary photographic plate, and the absorption spectrum is determined with a sensitive thermopile which absorbs the heat rays and converts them into electricity which is measured with a galvanometer.

Glass prisms and lenses are satisfactory for visible light, whereas quartz is generally used for the ultra violet, and rock salt for the infra red. In each case the apparatus must be transparent to the light which is being used.

Various units are used for measuring the wave-length as shown in the following table.

UNITS OF WAVE-LENGTH

Unit	Symbol	Millimeters	Centimeters
Micron.....	μ	one-thousandth	10^{-4}
Millimicron.....	mμ	one-millionth	10^{-7}
Ångström.....	Å	one-ten-millionth	10^{-8}

Light is described also in *wave-numbers* which are expressed in reciprocal centimeters. For example, ultra-violet light of 250 mμ or 2500 Å has a wave-length of 2.5×10^{-5} cm. and a wave-number of $\frac{1}{2.5 \times 10^{-5}}$ or 40,000 reciprocal centimeters. In some of the earlier work reciprocal millimeters were used. The *frequency* of light is obtained by dividing the velocity of light (3×10^{10} cm. per sec.) by the wave-length. Thus light of 2500 Å or 2.5×10^{-5} cm. has a frequency of $\frac{3 \times 10^{10}}{2.5 \times 10^{-5}} = 1.2 \times 10^{15}$ sec.$^{-1}$. Wave-numbers are usually used for studying absorption and emission spectra, but frequencies are used in photochemistry. Ångström units are widely used in physics.

If a solvent is used for dissolving the colored material, it must not of itself exhibit absorption in the region to be examined, and the same solvent should be used throughout a series of experiments because a solvent sometimes causes a shift of the absorption bands of the dissolved material.

The absorption of light by a solution changes with the thickness of the layer and with the concentration in a manner which is characteristic for each absorbing material. Sometimes the spectrum is photo-

graphed at a number of different concentrations and the region of absorption gradually narrows as the solution is diluted. The wave-length of the last part of the absorption band to fade out is noted.

Sometimes the thickness is varied while the concentration remains constant; the convenient device of Baly for altering the length of the

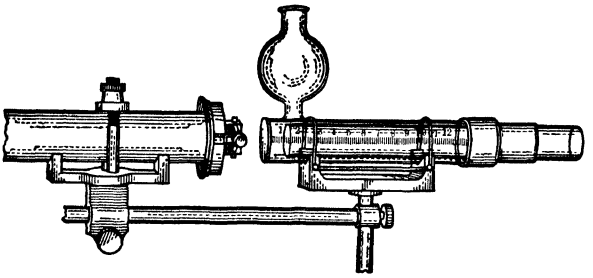


FIG. 42

absorbing column of liquid is shown in Fig. 42. It consists of two closely fitting tubes, one end of each tube being closed by a plane, quartz disc. The outer tube is fitted with a small bulbed-funnel and is graduated in millimeters. The two tubes are joined by means of a piece of rubber tubing which prevents leakage of the contents, and at the same time admits of the adjustment of the column of liquid to the desired length simply by sliding the smaller tube in or out. In this manner it is possible to record on a single photographic plate an entire series of spectra showing the change in absorption resulting from a progressive diminution in the number of absorbing molecules in the path of the incident radiation.

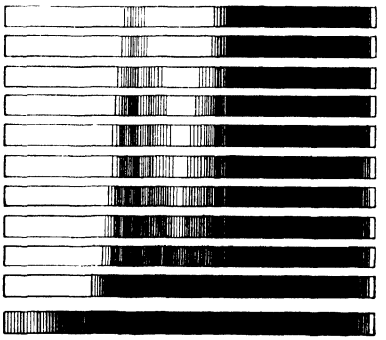


FIG. 43

In Fig. 43 is shown a series of absorption spectra of ten different thicknesses of a solution of sulphanilic acid in water. The uppermost spectrum corresponds to a 50-mm. column of 0.001 *m* $NH_2 \cdot C_6H_4 \cdot SO_3H$; the succeeding strips represent the absorption spectra resulting from diminishing the thickness of the absorbing layer by uniform steps of 5 mm. The lowest spectrum is that of the source of light alone. Applying a scale of wave-lengths, or making use of a curve of calibration of the prism of the spectrograph, the positions of the limits of absorption are determined and laid off as abscissas against the logarithms of the

corresponding thicknesses in millimeters. In this manner the absorption curve shown in Fig. 44 is obtained. The logarithm of the thickness rather than the thickness is usually plotted in order to cover a greater range. It will be seen from the diagram that the maximum absorption occurs at a wave-number of 35,800.

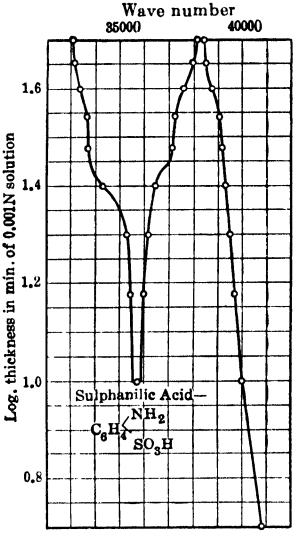


FIG. 44

The quartz spectrograph, with which the absorption spectra shown in Fig. 43 were obtained, is represented diagrammatically in Fig. 45. Light from a suitable source *A* is concentrated upon the slit *S* of the spectrograph by means of a quartz condensing lens *L*. The solution to be examined is placed in the absorption tube *C* and then interposed between *A* and *S*. After traversing the solution, the rays of light enter the slit of the collimator of the spectrograph where, by means of a quartz lens, they are rendered parallel before striking the quartz prism *P*. The latter consists of two 30° half-prisms placed face to face, one prism being cut from a right-handed, and the other from a left-handed, crystal of quartz in such a manner as to bring the optic axis parallel to the base of each half-prism. This type of prism was devised by Cornu in order to eliminate the doubling effect due to the polarizing action of quartz on the emergent beam. The refracted and dispersed rays then enter the camera *B* where the spectrum is photographed on the plate *D*. The plate holder is fitted

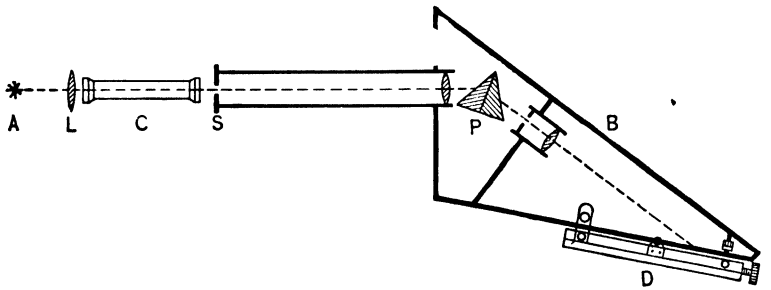


FIG. 45

with a rack and pinion by means of which the plate may be moved through measured distances in a vertical plane, thus enabling the experimenter to photograph a number of spectra on the same plate.

The instrument may also be provided with a specially calibrated, transparent wave-length scale which can be brought in direct contact with the plate and photographed above or below the spectra as desired. This device enables one to read the wave-lengths corresponding to the limits of absorption directly from the plate, thus avoiding the necessity of preparing a special calibration curve for the instrument.

The source of light to be employed varies with the character of the investigation; in some cases an iron arc proves satisfactory and in other cases a condensed spark between suitable electrodes is preferable.

Spectrophotometry. The intensity of light, I, after passing through a uniformly absorbing medium depends on the intensity of the incident light I_0 and the thickness, l, as given by Lambert's law. It is expressed by the following formula

$$k = \frac{1}{l} \ln \frac{I_0}{I}, \tag{14}$$

where k is a constant, known as the *absorption coefficient*, which depends on the nature of the material and the wave-length of light. This formula is derived with the help of integral calculus* from the experimental fact that the rate of decrease in intensity with thickness is proportional to the intensity of the light, as given by the differential equation

$$-\frac{dI}{dl} = kI. \tag{15}$$

The logarithmic equation (14) may be written in the exponential form

$$I = I_0 e^{-kl}. \tag{16}$$

These equations are often written with common logarithms, and in place of the constant k, a constant E is used, as given by equation (17).

$$E = \frac{1}{l} \log \frac{I_0}{I}. \tag{17}$$

E is called the *extinction coefficient*; it may be defined as the reciprocal of that thickness which reduces the intensity of the transmitted light to one-tenth of its original value. When a thickness of 1 cm. (or one unit) reduces the light to one-tenth of its intensity, E has a value of 1 and k has a value of 2.303.

The magnitude of the absorption constant, or extinction coefficient

* Details of this simple integration are given in " Mathematical Preparation for Physical Chemistry," p. 132.

is measured experimentally with a spectrophotometer; it offers the best way of describing quantitatively the nature of the absorption.

One of the most satisfactory instruments for spectrophotometric measurements in the visible region of the spectrum is that designed by Nutting.* The Nutting spectrophotometer as used in conjunction with a constant deviation wave-length spectrometer, is shown in Fig. 46. The light from a small incandescent lamp L, enclosed in a suitable housing, is split into two parallel beams by means of the two prisms P, P'. One of the beams then passes through the cell, C, containing the absorbing solution, while the other traverses an exactly similar cell

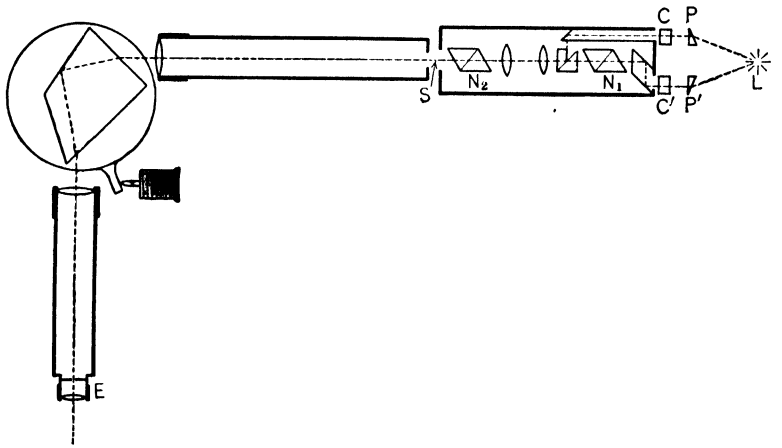


FIG. 46

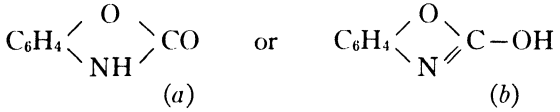
containing the solvent. Both beams then enter the photometer, the lower beam traversing the Nicol prism, N_1, where it becomes polarized, while the upper beam is brought into close juxtaposition with the lower beam by means of reflecting prisms. Both upper and lower beams then traverse a second Nicol prism, N_2, before they emerge from the photometer. The construction of the instrument is such that there is projected upon the slit, S, of the constant deviation wave-length spectrometer, a double field, one half of which is illuminated by the light which has undergone absorption by the solution in C and traversed the Nicol prism, N_2, while the other is illuminated by the light which has passed through the solvent and both Nicol prisms, N_1 and N_2. Since the light which has traversed the solvent and the Nicol prism N_1 is polarized, its intensity can be altered by rotating the prism N_2. On observing the resulting spectrum in the eye-piece E of the spectrometer, one sees a spectrum divided into two horizontal strips in close juxtapo-

* Nutting, Bull. Bureau of Stand., **7**, 239 (1910).

sition, one of which is reduced in intensity in consequence of the absorption of the solution. The intensity of the other strip can be reduced to match that of the first, for any portion of the spectrum, by rotating the Nicol prism N_2. Attached to the latter is a divided circle (not shown in the diagram) which is graduated to give the values of $\log I_0/I$ directly. When a perfect match is obtained for a particular wave-length, the value of the extinction coefficient is easily determined by dividing the reading on the graduated circle by the thickness of the absorbing layer in centimeters.

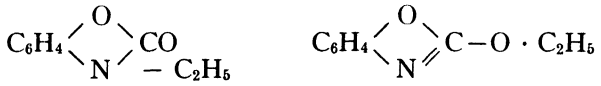
In ultra-violet spectrophotometry a beam of light is split into two parts as just described and the two spectra are photographed simultaneously, one above the other. An iron arc or other source with many emission lines is used, and one beam passes through the absorbing liquid and the other through a rotating sector wheel or special Nicol prism so that its intensity can be reduced. The intensity of the reference beam is reduced progressively and the logarithms of the intensity ratios, $\log I_0/I$, are plotted against the wave-lengths at which the two spectra are of equal intensity.

Absorption and Constitution. The systematic investigation of the ultra-violet absorption spectra of organic compounds has proved of great value in establishing the structure of numerous compounds of uncertain chemical constitution. The importance of this type of research has been abundantly demonstrated by the results of the investigations of Hartley, Baly, Desch, and others. A few illustrations of the relation of absorption bands to chemical constitution must here suffice. We will take the case of *o*-hydroxy-carbanil; the constitution of this substance was known to be represented by one of the two following formulas: —*



(*a*) (*b*)

The formulas of the ethyl derivatives of this compound are known to be as follows: —



Lactam ether Lactim ether

On comparing the absorption bands for the three substances (Fig. 47), it is apparent that the curves for the lactam ether and *o*-hydroxy-

* Hartley, Dobbie and Paliatseas, J. Chem. Soc., **77**, 839 (1900).

carbanil bear a close resemblance to each other, while the curve for the lactim ether is very different from the curves for the other two substances. The constitution of *o*-hydroxy-carbanil must then be very similar to that of the lactam ether. Hartley concluded, therefore, that formula (*a*) represents the structure of the molecule of *o*-hydroxy-carbanil.

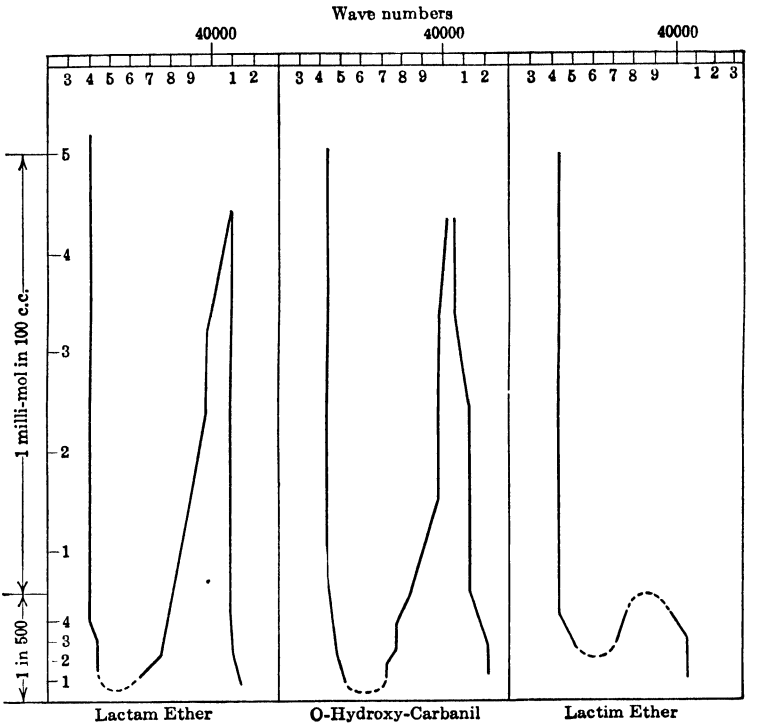


FIG. 47

Dielectric Constants and Dipole Moments. Faraday discovered that the attraction or repulsion between two electric charges varies with the nature of the intervening medium, or dielectric. If q_1 and q_2 represent two charges which are separated by a distance r, the force of attraction or repulsion, f, is given by the equation,

$$f = \frac{1}{D} \cdot \frac{q_1 q_2}{r^2}, \tag{18}$$

where D is a specific property of the medium known as the *dielectric constant*. The dielectric constant of air is taken as unity.

It is possible to split up the effect of the applied field into two factors, one due to deformation of the molecules and the other due to orienta-

tion of the molecules. The slight effect due to displacement of the atoms within the molecule is practically negligible. The effect due to orientation determines the magnitude of the dipole moment μ, a quantity which has been found valuable in deciding questions of molecular structure.*

Debye has given the fundamental formula

$$P = \frac{D-1}{D+2}\frac{M}{d} = \frac{4\pi N}{3}\alpha + \frac{4\pi N}{3}\frac{\mu^2}{3kT} \qquad (19)$$

where P is the molar polarization, M is the molecular weight, d the density and N the Avogadro number: α is the induced moment, a constant which is characteristic for each substance. k is the gas constant per molecule, or Boltzmann constant, obtained by dividing the molar gas constant R by the Avogadro number N, and has the value 1.372×10^{-16} erg per degree. It appears frequently in calculations of theoretical physics. The molar polarization $\frac{D-1}{D+2}\frac{M}{d}$ will be recognized as the Lorenz-Lorentz formula for molar refraction in which D has been substituted for n^2, where n is the refractive index of light. According to the electromagnetic theory of light $D = n^2$, at least for long waves. The term $\frac{4\pi N}{3}\alpha$ is the polarization produced by the applied field irrespective of the orientation effect. The term $\frac{4\pi N}{3 \times 3k}\frac{\mu^2}{T}$ is a measure of the moment produced by the unsymmetrical molecules aligning themselves between the charged plates in such a way that the positive parts of the molecules are attracted toward the negative plate and the negative toward the positive plate. This orientation is opposed by the kinetic motion of the molecules which is in turn a function of the absolute temperature. The other terms are constant, and it is thus possible to obtain the value of the dipole moment, μ, by plotting the molar polarization, P, against the reciprocal of the absolute temperature.

$$\text{Then } \mu = \sqrt{\frac{9k}{4\pi N} \times \text{slope}} = 0.0127 \times 10^{-8} \times \sqrt{\text{slope.}}$$

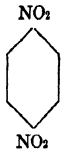
This method is particularly suitable for gases.

It is also possible to obtain the dipole moment of a substance by dissolving it in a non-polar solvent, measuring the dielectric constant, the refractive index, and the density of the solution at different concentrations, and extrapolating to infinite dilution.

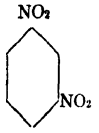
* J. W. Williams, Fortschritte der Chem., Phys. u. physik. Chem., **20**, (5), 1–66, (1930). C. P. Smyth, Chem. Rev., **6**, 549 (1929). J. W. Williams, Chem. Rev., **6**, 589 (1929). Polar Molecules. Debye.

The measurement of the dipole moment appears to be one of the best methods for obtaining a quantitative measure of the polarity of a molecule — i.e., the extent to which the positive and negative parts of the molecule are unsymmetrically arranged around the center of gravity. For example carbon tetrachloride has a moment of zero, whereas chloroform has a moment of 1.1. The case of the di-nitrobenzenes is interesting.

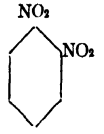
Benzene
$\mu = 0$



para di-nitrobenzene
$\mu = 0.3$



meta di-nitrobenzene
$\mu = 3.8$



ortho di-nitrobenzene
$\mu = 6.0$

The dielectric constants and dipole moments of various liquids and gases are given in the following table.

DIELECTRIC CONSTANTS AT 18° C.

Substance	D	$\mu \times 10^{18}$
Hydrogen peroxide	92.8	....
Water	77.0	1.84
Formic acid	63.0	1.64
Methyl alcohol	33.7	1.64
Ethyl alcohol	25.8	1.63
Ammonia, liquid	22.0	1.50
Chloroform	5.0	1.05
Ether	4.35	1.14
Carbon tetrachloride	2.25	0
Benzene	2.28	0
cis CHCl : CHCl		1.85
trans CHCl : CHCl		0

The development of electron tubes and radio technique has provided a new and accurate means for the experimental determination of dielectric constants.* The importance of these constants will become more apparent in subsequent chapters, especially in those devoted to electrochemistry.

* Daniels, Mathews and Williams, " Experimental Physical Chemistry," p. 248.

REFERENCES

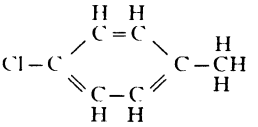
The Relations between Chemical Constitution and Some Physical Properties. Smiles.
The Molecular Volumes of Liquid Chemical Compounds. Le Bas.
Optical Rotation of Organic Substances. Landolt (translated by Long).
Spectroscopy. Baly.
Études de Photochimie. Victor Henri.
The Parachor and Valency. Sugden.
Polar Molecules. Debye.
Dielectric Constant and Molecular Structure. Smyth.

PROBLEMS

1. Calculate the volume occupied by a mol of ethyl butyrate at its boiling-point. The experimentally determined volume is 149.1 cc.

2. The density of methyl propionate ($C_2H_5COOCH_3$) at its boiling-point is 0.8463. What is its molar volume? What is the value calculated from the atomic volumes?

3. Estimate the density (grams per cc.) of chloroform ($CHCl_3$) at its boiling-point.

4. Para chlor toluene $ClC_6H_4CH_3$ or 

has a surface tension of 32.24 dynes per cm. at 25°. Its density at this temperature is 1.065.

a. Neglecting the density of the vapor at this temperature, what is the value of the parachor?

b. What is the value calculated from the atomic and structural parachors given on p. 89? *Ans.* (*a*) 283.

5. For propionic acid $d = 1.0158$ and $n = 1.3953$. Calculate the molar refraction and compare it with the sum of the atomic refractions (propionic acid is C_2H_5COOH).

6. Chloroform, $CHCl_3$, has an index of refraction of 1.4467 and its density at 20° is 1.489. What is its molar refraction? What is the value calculated from the atomic refractions?

7. In a Pulfrich refractometer having a prism of refractive index 1.621, the angle of emergence from CCl_4 was found to be 44° 39′. What is the index of refraction of CCl_4?

8. Calculate the refractive index of ethyl bromide (C_2H_5Br) at 20° from the table of atomic refractions. The density is 1.430.

9. An aqueous solution of maltose containing 13 g. in 100 cc. was examined in a polarimeter having a cell 20 cm. in length and found to have a rotation of 34°. What is the specific rotation of maltose? Another solution of maltose gave a rotation of 42.5° in a cell 10 cm. long. What is the concentration in grams per liter?

CHAPTER VI

ELEMENTARY PRINCIPLES OF THERMODYNAMICS*

Scope of Thermodynamics. Thermodynamics treats of the quantitative relations between heat and other forms of energy. It is important since all other forms of energy tend to change into heat and the quantitative measure of this tendency leads to important physical and chemical relations. Because thermodynamics is based on the statistical behavior of large numbers of molecules and because it is not concerned with the time variable, the laws of thermodynamics are quite exact and thorough mathematical treatment is possible.

Thermodynamics has been used in physics for a hundred years and it has found extensive applications in engineering but its practical importance in chemistry has developed only within the last few years. In this chapter the first two laws of thermodynamics will be presented

* This chapter involves the calculus, and the following formulas are used:

$$\frac{d \ln x}{dx} = x^{-1} \quad \text{or} \quad \frac{dx}{x} = d \ln x$$

$$\int \frac{dx}{x} = \ln x + \text{constant}$$

$$\int_{x_1}^{x_2} \frac{dx}{x} = [\ln x]_{x_1}^{x_2} = \ln x_2 - \ln x_1 = \ln \frac{x_2}{x_1}$$

$$\int x^{-2}\, dx = -x^{-1} + \text{constant}$$

$$du = \frac{\delta u}{\delta x} dx + \frac{\delta u}{\delta y} dy + \frac{\delta u}{\delta z} dz + \cdots$$

An increment, Δx, represents a small increase in x; $-\Delta x$ represents a small decrease in x. A differential, dx, represents an infinitesimal increase in x. A derivative, dy/dx, is the limit which the ratio $\Delta y/\Delta x$ approaches as Δx approaches zero. A partial differential, δx, represents an infinitesimal increase in the variable x while other independent factors are kept constant. Σ indicates a summation of finite increments; and $\int$ indicates a summation of infinitesimals. In chemistry log x is understood to mean $\log_{10} x$ (common logarithms) and ln x or $\log_e x$ is used for natural logarithms, hence

$$\ln x = 2.303 \log x.$$

These and other applications of calculus used in this book are treated in an elementary manner in Daniels' " Mathematical Preparation for Physical Chemistry," Differential Calculus on pp. 70–74; Integral Calculus on pp. 114–118; Partial Differentiation on pp. 174–180.

because they constitute a necessary background for much of the material coming later, but their applications to strictly chemical problems, and a discussion of entropy and the third law, will be deferred until after the study of chemical equilibria.

Energy. Since thermodynamics deals with energy and its transformations it is essential to have a clear understanding of the meaning of the term "energy." Energy may be defined as the capacity of a body, or system, to perform work. Since the work done affords a measure of the energy expended, it follows that both energy and work are to be measured in terms of the same unit, the *erg*. Energy stored in a system by virtue of its motion is known as *kinetic energy*. This definition applies equally to the motion of the molecules constituting a system and to the motion of the system as a whole. Energy stored in a system by virtue of its position is called *potential energy*. The energy contained in a body by virtue of its temperature and molecular structure, or the sum of its internal kinetic and potential energies, is known as its *intrinsic energy*. Since the deductions of thermodynamics are independent of any molecular hypothesis, we are not so much concerned as to whether the energy of a system is kinetic or potential, as we are with the determination of the gain or loss in energy which the system may experience in undergoing a given transformation.

Although we may employ algebraic symbols to represent the total energy stored in a system, it should be borne in mind that we possess no means of measuring this energy. When a process occurs in which the energy of a system undergoes change, our measurements merely give us the gain or loss in the energy of the system as a result of the change. For example, let a body having a mass of 1 gram fall, under the influence of gravity, through a distance of 1 meter; the resulting loss in potential energy is 1 g. $\times$ 981 cm./sec.^{2} $\times$ 100 cm. = 98,100 ergs. In this calculation, the absolute values of the potential energy of the body in its initial and final states are not involved, and all that we have learned is that in its final state the body possesses 98,100 ergs less potential energy than it possessed in its initial state.

It will be remembered that in the c.g.s. system a dyne is a force which gives to a mass of 1 gram an acceleration of 1 cm. per sec. per sec. An erg is the energy produced by 1 dyne acting through 1 centimeter. A joule is 10^7 ergs. The force of gravity is about 980.6 dynes, depending slightly on the latitude and the elevation above sea-level.

All forms of energy may be expressed as the product of two factors — an intensity factor and a capacity factor. Examples are given in the following table:

Energy	Intensity	Capacity
linear (ergs)	force (dynes)	distance (cm.)
kinetic (ergs)	$\frac{1}{2}$ velocity^2 (cm. per sec.)	mass (grams)
volume (ergs)	pressure (dynes per sq. cm.)	volume (cc.)
heat (joules)	temperature (°C.)	heat capacity (joules per degree)
electrical (joules)	potential (volts)	coulombs (amperes × seconds)

It is evident that the different energies may be compared but that no relation exists between the intensity factors alone or between the capacity factors alone. For example, electrical energy may be converted quantitatively into heat energy but the rise in temperature cannot be calculated from the voltage unless the quantity of the electrical energy and the heat capacity of the system are known. It follows also that the same quantity of energy may be generated by a small quantity of water passing through a turbine from a great height as from a large quantity of water falling through a short distance.

The First Law of Thermodynamics. The first law is merely a statement of the principle of the conservation of energy, according to which energy cannot be created nor destroyed. In other words, the sum of all the energies in an isolated system remains constant. This fundamental principle was first clearly formulated by Mayer in 1842 shortly after the publication of important investigations by Helmholtz, Joule, Hirn, and others on the transformation of work into heat and heat into work. Subsequently many exact experiments have proved conclusively that mechanical work may be transformed completely into heat. In some of these experiments a measured amount of work was used in stirring a liquid and the rise in temperature was measured, and in others a known quantity of electricity was passed through a heating coil immersed in a liquid containing a thermometer. The best determinations show that 4.185 joules of energy correspond to 1 calorie (15° calorie), and this quantity is known as the mechanical equivalent of heat.

Our confidence in the first law of thermodynamics rests largely on the fact that no exceptions to it have yet been found and no perpetual motion machine has ever been invented. At first sight one might think that the energy expended in lifting a piece of iron is destroyed when the iron is dissolved in sulphuric acid, but the iron in the resulting

ferrous sulphate is at a higher level and possesses potential energy equal to the energy expended in the lifting. If energy is expended in coiling a steel spring and the spring is dissolved in acid the energy appears to be lost, but it is certain that more heat is evolved by a coiled spring than by an uncoiled spring. The difference is so small, however, that it has not yet been detected by present calorimetric methods. Even the new developments in relativity do not contradict the first law if one considers matter to be a form of energy, and the large evolution of energy produced by the condensation of four hydrogen atoms to give a helium atom is presumably offset by the actual decrease in mass. This process is thought to be going on in stellar spaces and giving rise to cosmic radiation.

A change in energy of a system may be brought about in three different ways: the system may do work, it may absorb heat, and it may undergo an increase in internal energy. The absolute value of the internal energy U cannot be determined because it depends on many factors as yet unknown, but the change which it undergoes in passing from state 1 to state 2 can be measured and

$$\Delta U = U_2 - U_1. \tag{1}$$

The work done by the system on its surroundings, as in the case of an expanding gas, is termed w; and $-w$ is then the work done by the surroundings on the system. Heat absorbed by the system from its surroundings is designated by q; and heat evolved is then $-q$. According to the principle of the conservation of energy the total effect, considering both the system and its surroundings, is constant, and

$$\Delta U = q - w. \tag{2}$$

In many cases electrical work, and work done against surface forces, are excluded and the only work done is that of expansion against a pressure, and then

$$w = p(v_2 - v_1) = p\,\Delta v \tag{3}$$

and

$$\Delta U = q - p\,\Delta v. \tag{4}$$

If there is no change in the internal energy, ΔU becomes zero and the work done is exactly equal to the heat absorbed, i.e., $q = w$. This situation is illustrated by the expansion of a perfect gas.

If there is no change in volume $p\Delta v$ becomes zero and $\Delta U = q$. In this case the heat absorbed is numerically equal to the increase in internal energy; in other words, the heat evolved is equal to the decrease in internal energy. When zinc reacts in a closed bomb with sulphuric acid to produce zinc sulphate and hydrogen, the decrease

in internal energy, $-\Delta U$, is measured quantitatively by the heat evolved, $-q$.

The change in internal energy, ΔU, depends solely on the initial and final states of the system. The heat absorbed, q, and the work done, w, depend on the manner in which the process is carried out.

Heat Content. The decrease in internal energy may be determined by measuring the heat evolved at constant volume, as already explained. Most chemical reactions, however, are studied at constant pressure and it is convenient to use a different term, heat content, which is defined by the equation

$$H = U + pv. \tag{5}$$

Heat content is equal to the internal energy plus the product of pressure and volume. The absolute heat content of a system is not known but the difference between the heat content in the final state H_2 and heat content in the initial state H_1 can readily be measured.

$$\Delta H = H_2 - H_1 = U_2 + p_2v_2 - (U_1 + p_1v_1) = \Delta U + p_2v_2 - p_1v_1. \tag{6}$$

At constant pressure

$$\Delta H = \Delta U + p(v_2 - v_1) = \Delta U + p\,\Delta v,$$

also

$$\Delta H = q_p \text{ since by the first law } q = \Delta U + p\,\Delta v. \tag{7}$$

The *decrease* in heat content $(-\Delta H)$ is thus determined very simply by measuring the heat evolved at constant pressure.

Heat Capacity. The mean heat capacity, c, of a system between any two given temperatures may be defined as the quantity of heat required to raise the system from the lower to the higher temperature divided by the difference between the two temperatures, or

$$c = \frac{q}{T_2 - T_1}, \tag{8}$$

where q is the quantity of heat absorbed and T_1 and T_2 are the initial and final temperatures, respectively. The heat capacity varies with the temperature, and so it is necessary to make the temperature interval very small. The true heat capacity at any given temperature may be defined by the differential expression,

$$c = \frac{q}{dT}.^{*} \tag{9}$$

* q represents a *change* in energy, i.e., a difference in energy content, which may be large or infinitesimally small. It is not necessary then in equations of this type to write dq. Capital C is used for molar heat capacity, and in general capital letters stand for molar quantities.

It is obvious that the magnitude of the heat capacity of a system will depend upon whether it is determined at constant volume, or at constant pressure. If the heat capacity is determined at constant volume, no external work will be performed and the heat absorbed will be a measure of the increase in the internal energy of the system. The heat capacity at constant volume per mol of substance, C_v, is, therefore, defined by the expression,

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v. \tag{10}$$

On the other hand, at constant pressure the heat absorbed is a measure of the increase in the heat content, and the heat capacity per mol of substance, C_p, is defined by the equation,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left[\frac{\partial}{\partial T}(U + pv)\right]_p. \tag{11}$$

Internal Energy of a Gas. It has been shown that any two of the three variables, temperature, pressure and volume, suffice to define the condition of a gas. The change in the internal energy of a gas may, therefore, be expressed by the fundamental equation of partial differentiation,

$$dU = \frac{\partial U}{\partial T}dT + \frac{\partial U}{\partial v}dv, \tag{12}$$

where temperature and volume are the chosen variables. The derivative $\frac{\partial U}{\partial T}$ represents the heat absorbed per degree by a mol of gas at constant volume and, therefore, according to equation (10), it may be replaced by C_v. Equation (12) now assumes the form,

$$dU = C_v dT + \frac{\partial U}{\partial v}dv. \tag{13}$$

But according to equation (2)

$$dU = q - w,$$

and consequently we have

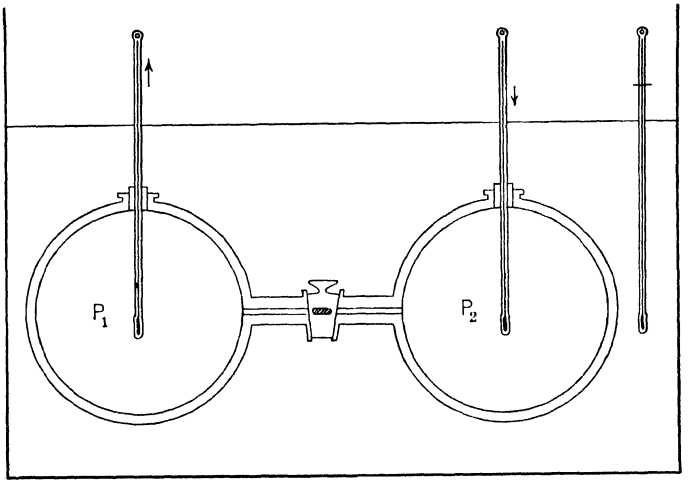
$$q = C_v dT + \frac{\partial U}{\partial v}dv + w. \tag{14}$$

The work of increasing the volume of a gas by an amount dv at constant pressure, p, is $p\,dv$. Hence equation (14) becomes,

$$q = C_v dT + \frac{\partial U}{\partial v}dv + p\,dv. \tag{15}$$

This equation means in words that the heat absorbed when a gas is heated very slightly is equal to the sum of three quantities: (1) the temperature increase multiplied by the heat capacity at constant volume; (2) the volume increase multiplied by the rate at which the internal energy increases with volume, all other factors being held constant; (3) the work done in expansion.

The Gay-Lussac-Joule Experiment. In order to determine whether a gas undergoes any change in temperature when it expands into a vacuum, Gay-Lussac, in 1807, carried out the following experiment



$P_2 > P_1$

FIG. 48

indicated in Fig. 48. Two large vessels of equal capacity and provided with thermometers, were connected by means of a stop-cock. One vessel was filled with gas, and the other was evacuated. On opening the valve and allowing the gas to expand into the evacuated vessel, the temperature of the gas in the vessel (P_2) was observed to fall. A corresponding rise in temperature occurred in the other vessel (P_1), due to the compression by the inflowing gas. When equilibrium of pressure had been established, the decrease of temperature in the first vessel was found to be exactly equal to the increase of temperature in the second vessel. From this, Gay-Lussac concluded that, taken as a whole, the gas showed no tendency to become warmer, or colder, during free expansion. A somewhat similar experiment was performed by Joule in 1844. He immersed two similarly connected vessels in a calorimeter, and found that no appreciable change in the temperature of the water of the calorimeter occurred during the free expansion of a gas, as

the heating in one vessel was exactly offset by the cooling in the other.

From these two experiments it is evident that, when a perfect gas expands freely into a vacuum, heat is neither evolved nor absorbed. Furthermore, the volume of the system as a whole remains constant, and, therefore, no external work is done. Since $q = 0$ and $w = 0$, in the equation $\Delta U = q - w$, it follows that $\Delta U = 0$, i.e., the *internal energy of a given mass of a perfect gas is independent of the volume.* Experiments by Joule and Thomson have shown that this statement is only approximately true for actual gases. A change in temperature does occur when a real gas expands freely, owing to the fact that a certain amount of work is required to overcome the mutual attraction of the molecules for each other. This phenomenon is known as the Joule-Thomson effect. For a perfect gas, however, in which no such attractive forces exist, the internal energy is independent of the volume.

The Joule-Thomson Effect. In their investigation of the departure of real gases from ideal behavior, Joule and Thomson conducted a series of important experiments on the thermal effects accompanying gaseous expansion. A continuous current of gas, under a constant pressure higher than that of the atmosphere, was forced through an insulated tube containing a porous plug of cotton or silk. The temperature of the gas was observed both before and after its passage through the plug, and, after introducing several corrections, the true temperature of the gas after expansion was determined. It was found that air, oxygen, nitrogen and carbon dioxide were all cooled by expansion, while with hydrogen a slight rise in temperature was found to occur. The essential features of the experiment are repre-

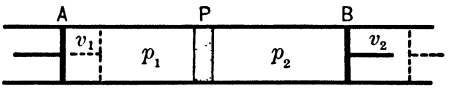


FIG. 49

sented diagrammatically in Fig. 49 in which P is the porous plug and A and B are two movable pistons. The work done in forcing a mol of gas at volume v_1 and pressure p_1 through the plug is p_1v_1. Similarly, on the opposite side of the plug, the work done by the gas in driving B outward against atmospheric pressure is p_2v_2. If the behavior of the gas is not ideal, the work done in expansion at the outlet will not be equal to the work done in compression at the inlet, external work will be performed by the system as a whole, and we may write

$$p_2v_2 - p_1v_1 = w.$$

If the system is thermally insulated and the process is adiabatic, $q = 0$, and we have, according to equation (2),

$$\Delta U = U_2 - U_1 = -w = p_1v_1 - p_2v_2,$$

or $$U_2 + p_2v_2 = U_1 + p_1v_1.$$

But $$U_2 + p_2v_2 = H_2, \quad \text{and} \quad U_1 + p_1v_1 = H_1,$$

hence $$H_2 = H_1.$$

It is apparent, therefore, that in the free expansion of a real gas, the heat content, and not the internal energy, remains constant. In consequence of this fact, the Joule-Thomson effect, k, may be defined mathematically by the expression,

$$k = \left(\frac{\partial T}{\partial p}\right)_H. \tag{16}$$

For air at atmospheric pressure and 0°, k has the value + 0.4, and a decrease in pressure of one atmosphere decreases the temperature 0.4° C. For hydrogen and helium at room temperature k has negative values, or in other words these gases become warmer when forced through a porous plug. At temperatures below 154° K., however, k becomes positive for hydrogen. It is evident that two factors are involved in the Joule-Thomson effect — an expansion against the force of attraction between the molecules (corresponding to a in van der Waals' equation), and a work term involving the change of pv with pressure as shown on p. 11.

The first effect always produces cooling; the second effect results in a temperature fall, if pv is larger at the lower pressure, or a temperature rise, if pv is smaller at the lower pressures. In hydrogen pv decreases at lower pressures and at room temperature this heating effect is greater than the cooling due to the first factor. At low temperatures, when the gas approaches the liquefaction point the attraction between the molecules becomes greater and the gas is then cooled when forced through a porous plug.

These qualitative considerations may be expressed more quantitatively with the help of partial differentiation as follows.

Since H is a single-valued function of any two of the three variables T, p and v, the general rule for partial differentiation may be applied; choosing temperature and pressure as the variables, we may write

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp. \tag{17}$$

But, in case of the free expansion of gas H is constant and $dH = 0$, so that on rearranging terms

$$\frac{dT}{dp} = \frac{-\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = \frac{-\left(\frac{\partial H}{\partial p}\right)_T}{C_p}. \tag{18}$$

Writing for H its equivalent $U + pv$

$$\frac{dT}{dp} = \frac{-\left(\frac{\partial (U + pv)}{\partial p}\right)_T}{C_p} = -\frac{1}{C_p}\left(\frac{\partial U}{\partial p}\right)_T - \frac{1}{C_p}\left(\frac{\partial (pv)}{\partial p}\right)_T. \tag{19}$$

In this equation $-\frac{\partial U}{\partial p}$ corresponds to the decrease in internal energy as the molecules are crowded closer together, a process which liberates heat and causes the temperature to rise if the system is thermally insulated. According to this term a *decrease* in pressure should produce a drop in the temperature.

Neglecting the term $-\frac{1}{C_p}\left(\frac{\partial U}{\partial p}\right)_T$ and considering only the last term of the equation, if pv increases when p decreases $\frac{dT}{dp}$ will have a positive value and the gas will tend to be cooled when the pressure is decreased by the passage of the gas through a porous plug. If pv decreases when p decreases $\frac{\partial (pv)}{\partial p}$ will be positive and $\frac{dT}{dp}$ will be negative indicating that the temperature will rise.*

Relation between the Two Specific Heats, C_p and C_v. It has already been proved that

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{and} \quad C_v = \left(\frac{\partial U}{\partial T}\right)_v.$$

Therefore,
$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v,$$

$$= \left[\frac{\partial (U + pv)}{\partial T}\right]_p - \left(\frac{\partial U}{\partial T}\right)_v,$$

$$= \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v. \tag{20}$$

* An exhaustive investigation of the Joule-Thomson effect in air has been carried out by Roebuck. Proc. Am. Acad. Art. Sci., **13**, 537 (1925).

But since U is a single-valued function of the variables T and v, it follows that

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv,$$

and therefore,

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p.$$

Substituting in equation (20) we obtain

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v. \tag{21}$$

But for a perfect gas $\left(\frac{\partial U}{\partial v}\right)_T = 0$.

Hence equation (21) becomes

$$C_p - C_v = p\left(\frac{\partial v}{\partial T}\right)_p, \tag{22}$$

and since $v = \frac{RT}{p}$, we may replace $\left(\frac{\partial v}{\partial T}\right)_p$ by $\frac{R}{p}$ and equation (22) then simplifies to

$$C_p - C_v = R. \tag{23}$$

This expression has already been derived in connection with the kinetic theory of gases (p. 27) but the method of partial differentiation is illustrated here because it is a powerful tool for developing important formulas of thermodynamics.

Reversible Cycles. When a gas increases in volume it pushes back the surrounding atmosphere and does work. Imagine that a liquid is placed in a cylinder provided with a weightless, frictionless piston and that it is set into a large reservoir at the boiling-point of the liquid. The fact that no machine can be built with a weightless, frictionless piston in no way affects the conclusions drawn from this idealized process. The vapor pressure of the liquid at this temperature is exactly equal to the atmospheric pressure and the whole system is in a state of equilibrium. If now the temperature of the reservoir is raised by an infinitesimal amount the vapor pressure of the liquid will be slightly greater and the piston will be pushed back against the atmospheric pressure. As more liquid evaporates the volume increases and the pressure in the cylinder is thus maintained constant; heat flows in from the reservoir to maintain the temperature constant and offset the cooling caused by vaporization.

The work done is the product of the pressure and the increase in

volume. If water is chosen as the liquid the temperature will be 100° C. and when 1 mol has been evaporated the increase in volume can be calculated on the assumption that the vapor behaves as an ideal gas and that the volume of the liquid (18 cc.) is negligible:

$$w = p\,\Delta v = 1 \times (22.4 \times 373/273) = 30.6 \text{ liter-atmospheres.}$$

Since it is assumed that the ideal gas laws are obeyed RT may be substituted for $p\Delta v$ and R may be taken in any units (p. 10) giving, at 373°, 30.6 liter-atmospheres or 742 calories. The work done depends only on the volume increase and is independent of the cross-section of the piston or the pressure of the gas. In very exact work it is not legitimate to consider a vapor at its boiling-point as an ideal gas.

The energy consumed in doing this work comes from heat absorbed from the reservoir by the evaporating liquid. A great deal more energy is absorbed, however, in separating the molecules from their neighboring molecules in the liquid. To vaporize a gram of water at 373° and atmospheric pressure 539 calories is required. This corresponds to 9710 calories per mol. Then under these conditions

$$q = \Delta H = \Delta U + p\,\Delta v. \tag{24}$$

$\Delta H = 9710$ and $p\Delta v = 742$, so that the change in internal energy, ΔU, must be 8968 calories.

This process of absorbing heat and doing external work is reversible in the example just given because at any time the vaporization can be stopped by an infinitesimal increase in pressure, making internal and external pressures exactly equal. By still further increasing the pressure by an infinitesimal amount the vapor can be made to condense and give back the heat of vaporization to the reservoir. A *reversible process*, then, is defined as one which may be reversed at will by making infinitesimal changes. A system undergoing a reversible change is always very nearly in a state of equilibrium. An irreversible process is one in which the successive steps of the direct process cannot be retraced. The more nearly reversible a process is the greater is the work which can be obtained from it, and the maximum work possible is obtained when the process is carried out reversibly. For this reason the reversible processes are particularly important in thermodynamics.

After a mol of water has been evaporated by decreasing the pressure it can be condensed again by increasing the pressure and thus the whole system is restored to its original condition. Such a process, which involves a series of changes and restores the system to its original condition, is called a *cycle*. A *reversible cycle* is one which is carried out by applying infinitesimal changes under conditions such

that the system is at all times practically in a state of equilibrium. Since in a reversible cycle the final and initial states are identical there can be no change in U or H, but q and w may vary with the nature of the cycle. If the reversible cycle is carried out at constant temperature as in the example just described the work required to restore the system to its original condition exactly offsets the work done by the system and in general the total work done in any reversible, *isothermal*, cyclic process is zero.

Isothermal and Adiabatic Expansion. When a gas expands, its temperature will fall, unless an amount of heat is supplied from its surroundings sufficient to compensate for the energy expended in the performance of external work. When this natural tendency of a gas to undergo cooling during free expansion is thus offset, and the temperature of the gas remains constant, the gas is said to expand *isothermally*.

When the temperature of a gas is maintained constant, by supplying heat during expansion, or abstracting heat during compression, the process is known as an isothermal process. On the other hand, when a gas undergoes expansion or compression, and it neither receives heat from nor imparts heat to its surroundings, the process is known as an adiabatic process. If a gas is compressed adiabatically, the temperature rises and tends to cause the gas to expand; this temperature effect opposes the compressing force and, therefore, more work is required to bring about a given change in volume by adiabatic compression than by isothermal compression. This becomes clear if we make use of the diagram shown in Fig. 50, in which pressures are plotted as ordinates, and volumes as abscissas. If a gas is compressed isothermally from volume v_1 to volume v_2, the work done will be represented by the area ABv_2v_1, whereas if it is compressed adiabatically, the work done will be represented by the area ACv_2v_1. It will be noticed that the slope of the adiabatic line, AC, is steeper than that of the isothermal line, AB.

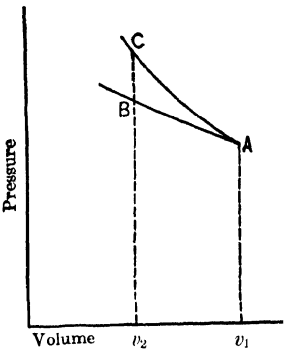


FIG. 50

Maximum Work. The maximum work which can be done by the *isothermal expansion* of a perfect gas is an important quantity in theoretical chemistry. Imagine a gas enclosed in a cylinder fitted with a frictionless and weightless piston and placed in a thermostat at the temperature T. The external pressure on the piston is decreased by a small amount, $-\Delta p$, and the gas expands by an amount, Δv. In this

expansion the pressure of the gas in the cylinder decreases until it becomes equal to the external pressure and then the piston ceases to rise. This process differs from the one described previously on page 119 where the gas was in contact with liquid at its boiling-point so that the pressure in the cylinder was maintained constant. A second decrease in pressure produces a second expansion Δv, and as the pressure is decreased in successive amounts the volume undergoes a series of expansions. In each little expansion the work done is the external pressure multiplied by Δv, and the total work done in expanding from the *initial* volume v_1 to the *final* volume v_2 is equal to the sum of the work done in each expansion, a fact which is represented by the equation:

$$w = \sum_{v_1}^{v_2} p\,\Delta v. \tag{25}$$

The total work w becomes larger and larger as Δv is made smaller, and it attains a maximum value in the limiting case where Δv approaches zero.

Calculus* is designed to give a true value for this limiting case and

$$w_{\max} = \int_{v_1}^{v_2} p\,dv. \tag{26}$$

Only in case the maximum work is done can there be sufficient energy stored up to compress the gas and restore the original conditions. Under the conditions of maximum work the internal pressure and external pressure can never differ by more than an infinitesimal amount, dp, and the system is then always practically in a state of equilibrium, that is, it is a reversible process.

If 1 mol of a perfect gas is taken, $pv = RT$, or $p = \frac{RT}{v}$ and

$$w_{\max} = \int_{v_1}^{v_2} \frac{RT}{v}\,dv. \tag{27}$$

Since R and T are constants, integration gives

$$w_{\max} = RT \int_{v_1}^{v_2} v^{-1}\,dv = RT \ln \frac{v_2}{v_1} = RT\ 2.303 \log \frac{v_2}{v_1}. \tag{28}$$

The maximum work may be calculated in terms of pressures instead of volumes since $p_1v_1 = p_2v_2$ and

$$w_{\max} = RT \ln \frac{p_1}{p_2}. \tag{29}$$

The maximum work, w, done by the gas in expansion is equal to the minimum work, $-w$, required to compress the gas, and this change of

* "Mathematical Preparation for Physical Chemistry," pp. 162–164.

sign is effected in the calculation by simply interchanging the limits of integration and using the smaller volume for the upper limit. In integrations, the upper limit always refers to the final state and the lower limit refers to the initial state. The signs then take care of themselves. Also in the use of ΔII and Δx, etc., the value in the initial state is always subtracted from the value in the final state. $\Delta x = x_{\text{final}} - x_{\text{initial}}$, and again the signs take care of themselves. If x_{final} is greater than x_{initial}, Δx has a positive valve; if x_{final} is smaller than x_{initial}, Δx has a negative value.

In the adiabatic expansion of a gas the temperature falls but there is no exchange of heat with the surroundings and $q = 0$. Then by the first law

$$\Delta U = q - w = -w = -p\,\Delta v.$$

But $dU = C_v\,dT$ (equation (13) and Gay-Lussac experiment), hence

$$C_v\,dT = -p\,dv. \tag{30}$$

Since for 1 mol of a perfect gas $pv = RT$, it follows that

$$C_v\,dT = -RT\frac{dv}{v} \tag{31}$$

and

$$C_v\frac{dT}{T} = -R\frac{dv}{v}. \tag{32}$$

If v_i is the volume of the gas at the initial temperature T_i and v_f is the volume at the final temperature T_f we have on integrating between limits

$$C_v \ln\frac{T_f}{T_i} = -R\ln\frac{v_f}{v_i} \tag{33}$$

According to this equation when 1 mol of a perfect gas having a heat capacity C_v expands adiabatically v_f is greater than v_i and accordingly T_f must be less than T_i. In other words the gas cools off. It is evident also that adiabatic compression of the gas produces an increase in temperature.

The Second Law of Thermodynamics. Although work can always be transformed into heat, it does not follow that heat can be transformed completely into work. The first law of thermodynamics merely specifies that, when heat is converted into work, a definite quantitative relationship exists between the heat converted and the work done, but it tells us absolutely nothing as to the amount of work which can be obtained from a given quantity of heat. It is to the second law of thermodynamics that we must turn for information as to

the limitations which experience has shown govern the transformation of heat into work. The second law, as stated by Clausius, is as follows: — "*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.*" In other words, heat cannot of itself pass from a colder to a hotter body, but tends invariably toward a lower thermal level. It should be clearly understood that this is in no way contradictory to the first law.

An analogy in hydraulics serves to emphasize the second law. A large body of water is incapable of doing work until it can flow down to a lower level through some kind of a machine. In the same way a quantity of heat, unless aided by an external agency, can do work only by falling through a drop in temperature. It is evident that there is a great deal of heat in the ocean but that it cannot be converted into work because a lower temperature level is not readily available. The greater the drop in temperature the greater the fraction of heat which may be converted into work, as will be shown quantitatively in the next section.

A kinetic explanation is helpful. If one end of a tube of gas is hot and the other end cold, heat will flow from the hot end to the cold and in so doing work could be done. But after the motions of molecules have become averaged throughout, and the whole tube is at a uniform temperature, it is extremely improbable that the more rapidly moving molecules would all move spontaneously to one end causing the tube to become hot at one end and cold at the other. In fact it is far less likely than that a pack of cards after being shuffled should by continued shuffling return to the original order. It is less likely because the number of molecules is much greater than the number of cards in a pack and the laws of probability hold better when large numbers are involved.

The second law of thermodynamics may be applied to a variety of phenomena. It may be stated in a more general way as follows: *All systems tend to approach a state of equilibrium.* The movement of molecules of a dissolved substance from a region of high concentration to a region of low concentration until the concentration is uniform throughout the whole solution is merely another manifestation of the second law. The running down of a clock or the reaction of zinc and sulphuric acid are other illustrations.

The second law is a statistical law, and like all statistical laws it breaks down when only a small number of individuals is involved. For example, if there are more small particles moving around on one side of a microscopic field than on the other side the general tendency is

for particles to migrate from the region of high concentration to the region of low concentration until the concentration is uniform throughout, but every once in a while it will be observed that a particle moves in the opposite direction in violation of the second law. Progress has been made recently in theoretical physics by realizing that statistical laws do not necessarily apply to the behavior of individual molecules, electrons and quanta.

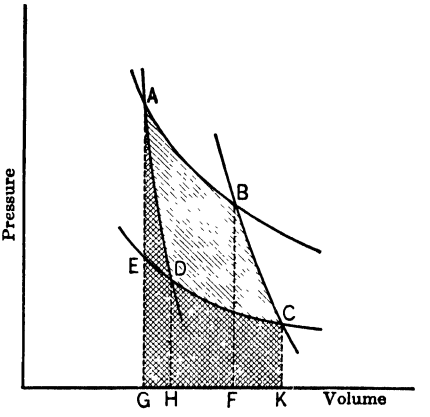


FIG. 51

Carnot's Cycle. In establishing the law which determines quantitatively the maximum quantity of heat which can be converted into work, Carnot made use of an imaginary engine operating through a reversible cycle as indicated in Fig. 51. In the present derivation 1 mol of a perfect, monatomic gas is enclosed in a cylinder with a weightless, frictionless piston and subjected to the following four successive steps, each of which has already been studied in detail.

1. AB represents isothermal, reversible expansion from v_A to v_B at temperature T_2.

$$w_{AB} = \text{area } ABFG = RT_2 \ln v_B/v_A \tag{34}$$
$$q_{AB} = w_{AB}.$$

2. BC represents adiabatic expansion from v_B to v_C. The temperature drops from T_2 to the lower temperature T_1. No heat is transferred and the energy for doing the work must come from the cooling of the gas, ΔU.

$$q_{BC} = 0$$
$$w_{BC} = \text{area } BCKF = C_v (T_2 - T_1) \tag{35}$$

also
$$C_v \ln \frac{T_1}{T_2} = -R \ln \frac{v_C}{v_B} \quad \text{(adiabatic expansion).} \tag{36}$$

3. CD represents isothermal, reversible compression from v_C to v_D at temperature T_1.

$$w_{CD} = \text{area } CDHK = RT_1 \ln v_D/v_C$$
$$w_{CD} = q_{CD}. \tag{37}$$

4. DA represents adiabatic compression from v_D to v_A. The temperature rises from T_1 to T_2.

$$q_{DA} = 0$$

$$w_{DA} = \text{area } DAGH = C_v(T_1 - T_2) = -C_v(T_2 - T_1) \quad (38)$$

also

$$C_v \ln T_2/T_1 = -R \ln v_A/v_D. \quad (39)$$

The gas is now at its starting point under the original conditions of temperature, pressure and volume and the four steps constitute a reversible cycle. Work done by the system, w, is shaded from left to right in the diagram and work done on the system by its surroundings is shaded from right to left. More work is obtained at the higher temperature than is required at the lower temperature and the net work is represented by the area $ABCD$. To offset this surplus work a quantity of heat is transferred from a higher temperature T_2, to a lower one, T_1. This work represents the maximum work obtainable because the cycle is reversible.

The total work, w, is as follows:

$$w = w_{AB} + w_{BC} + w_{CD} + w_{DA} = RT_2 \ln v_B/v_A + C_v(T_2 - T_1) + RT_1 \ln v_D/v_C + (-C_v(T_2 - T_1))^* \quad (40)$$

$$w = RT_2 \ln v_B/v_A + RT_1 \ln v_D/v_C = RT_2 \ln v_B/v_A - RT_1 \ln v_C/v_D. \quad (41)$$

In order to obtain a further simplification the last equations of steps 2 and 4 are compared,

$$\frac{C_v}{R} \ln \frac{T_1}{T_2} = -\ln \frac{v_C}{v_B} \quad (42)$$

and

$$\frac{C_v}{R} \ln \frac{T_2}{T_1} = -\ln \frac{v_A}{v_D} \quad (43)$$

or

$$\frac{C_v}{R} \ln \frac{T_1}{T_2} = -\ln \frac{v_D}{v_A}. \quad (44)$$

Obviously,

$$\frac{v_C}{v_B} = \frac{v_D}{v_A} \quad (45)$$

and rearranging

$$\frac{v_C}{v_D} = \frac{v_B}{v_A} \quad (46)$$

and substituting equation (46) into equation (41)

$$w = RT_2 \ln \frac{v_B}{v_A} - RT_1 \ln \frac{v_B}{v_A}. \quad (47)$$

* It will be noted that all the work terms are *added* and that the relative magnitudes of the final and initial states determine the sign.

Dividing this equation by, $q_{AB} = RT_2 \ln v_B/v_A$, as given in the first step

$$\frac{w}{q_{AB}} = \frac{R(T_2 - T_1) \ln \frac{v_B}{v_A}}{RT_2 \ln \frac{v_B}{v_A}} = \frac{T_2 - T_1}{T_2}. \tag{48}$$

Writing q_2 instead of q_{AB} for the heat absorbed at the higher temperature T_2, and remembering that the work is maximum work because the cycle is reversible,

$$w_{\max} = q_2 \frac{T_2 - T_1}{T_2}. \tag{49}$$

For infinitesimal changes in temperature

$$dw_{\max} = q \frac{dT}{T}. \tag{50}$$

This is a very important equation which may be regarded as a quantitative expression of the second law of thermodynamics. The ratio of work done to heat absorbed, w/q_2, is known as the efficiency of a process. This equation states that the maximum efficiency of a process involving heat transfer is equal to the drop in temperature divided by the temperature at which the heat is absorbed, or in other words it is equal to the drop in temperature divided by the maximum possible drop to absolute zero. (Temperatures in thermodynamics always refer to the absolute scale.)

This equation finds important practical applications in engineering. For example, it is desired to know what is the maximum work that can be obtained from 1000 calories supplied to a boiler at 100° C. if the condenser is at 20° C.

$$w_{\max} = 1000 \frac{373 - 293}{373} = 214 \text{ cal.} = 895 \text{ joules.}$$

If now the boiler temperature is raised to 150° C. by using higher compression, more work can be obtained for the same consumption of fuel.

$$w_{\max} = 1000 \frac{423 - 293}{423} = 307 \text{ cal.}$$

It is evident at once why gas engines operating with explosion temperatures many hundred degrees above the boiling-point of water are more efficient than steam engines. Mercury engines have been successfully operated, and their thermodynamic efficiency is high because the boiler temperature is 723° K.; but the advantage is offset by the initial cost of mercury, the great weight and the danger from poisoning.

The work done in a Carnot engine operating between T_2 and T_1 is the maximum work and it is equal to the work done in any *reversible* cycle operating between these two temperatures. If one machine were more efficient than another, work could be done with the more efficient one and the heat returned to the higher temperature with the less efficient one in such a way that work could be created in violation of the first law of thermodynamics. The Carnot cycle using an ideal gas is particularly significant because the absolute temperature scale is best defined in terms of work done thermodynamically, each degree rise producing the same amount of work by expanding a perfect gas. It is applicable to many of the phenomena of physical chemistry.

The Clapeyron Equation. A useful relation between vapor pressure, temperature and heat of vaporization was developed by Clapeyron. It may be developed in an *approximate* manner with the help of a simple thermodynamical cycle similar to Carnot's. One gram of a liquid at its boiling-point, T, is evaporated reversibly at atmospheric pressure in the manner previously described. When it is fully vaporized, the temperature is decreased very slightly by an amount ΔT and the pressure is decreased by an amount Δp. At this lower temperature $T - \Delta T$ the vapor is compressed again. When only the liquid remains the pressure is increased to p and the temperature to T. The liquid is thus returned to its initial conditions after going through a reversible cycle.

If v_2 is the volume in the gaseous state and v_1 is the volume of the liquid, the work done in vaporization is $p\ (v_2 - v_1)$ and the work done in compressing the vapor back to the liquid state is $(p - \Delta p)(v_1 - v_2)$.

Then, neglecting small effects, the total work w is given by the equation

$$\begin{aligned} w &= p(v_2 - v_1) + (p - \Delta p)(v_1 - v_2) \\ &= p(v_2 - v_1) - (p - \Delta p)(v_2 - v_1) = \Delta p(v_2 - v_1) \end{aligned} \tag{51}$$

and to offset this extra amount of work, $\Delta p(v_2 - v_1)$, done at the higher temperature, l calories, corresponding to the heat of vaporization per gram, is transferred from the higher temperature to the lower temperature.

Applying Carnot's cycle and the second law

$$w_{\max} = \Delta p(v_2 - v_1) = l\frac{\Delta T}{T} \tag{52}$$

or

$$\frac{\Delta p}{\Delta T} = \frac{l}{T(v_2 - v_1)}. \tag{53}$$

In this derivation certain quantities of heat and work are not included because they are small compared with the large values of w and l. The

smaller Δp and ΔT are made, the more nearly true does the above equation become and, in the limiting case, we have the more exact equation, which as a matter of fact can be derived rigorously in other ways,

$$\frac{dp}{dT} = \frac{l}{T(v_2 - v_1)}. \tag{54}$$

A similar formula can be obtained for the change of melting-point with pressure in which l represents the heat of fusion per gram, v_2 is the volume of the liquid and v_1 is the volume of the solid. In using this equation it is necessary to have the units consistent, i.e., the heat term must be expressed in the same units as the product of pressure and volume change. If the pressure is given in atmospheres and the volumes in cubic centimeters the heat may be expressed in cubic centimeter–atmospheres (1 cal. = 41.3 cc.–atmospheres); or the pressure may be converted into dynes when the heat is expressed in ergs.

Calculations involving these formulas may be illustrated with the following data. At 0° C. the heat of fusion of ice is 79.6 calories, or 3287 cc.–atmospheres, the density of water is 1.000 and the density of ice is 0.9106. The reciprocals of the densities 1.000 and 1.092 are the specific volumes or the volumes occupied by 1 gram. Then

$$\frac{\Delta p}{\Delta T} = \frac{l}{T(v_2 - v_1)} = \frac{3287}{273(1.000 - 1.092)} = -130.9.$$

In words, 130.9 atmospheres is the pressure required to lower the freezing-point of water 1°; and the reciprocal

$$-\frac{\Delta T}{\Delta p} = \frac{1}{130.9} = .0076$$

shows that an increase of 1 atmosphere lowers the freezing-point .0076°. The negative sign indicates that an increase of pressure causes a decrease in temperature, a relation which follows from the fact that the specific volume of ice is greater than that of water at the freezing-point.

The Clausius-Clapeyron Equation. Clausius showed how the Clapeyron equation may be simplified by assuming that the vapor obeys the ideal gas law. Taking 1 mol instead of 1 gram, V_2 is the volume of 1 mol of vapor, V_1 is the volume of 1 mol in the liquid state, and L is the molar heat of vaporization (molecular weight $\times$ l). Furthermore, V_1 may be considered negligible in comparison with V_2, as for

example in the case of water at 100° where V_1 is 18 cc. and V_2 is 30,600 cc. For V_2 may be substituted its equivalent RT/p. Then

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} = \frac{Lp}{RT^2}. \tag{55}$$

On rearrangement this becomes

$$\frac{1}{dT}\frac{dp}{p} = \frac{L}{RT^2} \tag{56}$$

or

$$\frac{d \ln p}{dT} = \frac{L}{RT^2}, \tag{57}$$

and integrating on the assumption that L and R are constants,

$$\int d \ln p = \int \frac{L}{R} T^{-2}\, dT, \tag{58}$$

$$\ln p = -\frac{L}{R}\frac{1}{T} + C \tag{59}$$

where C is the integration constant. This equation is linear in $\ln p$ and $1/T$, and when these quantities are plotted a straight line results the slope of which is numerically equal to $-L/R$. When logarithms to the base 10 are plotted the slope is $-L/2.303\,R$. We now have the theoretical justification for the empirical relation illustrated in Fig. 12 on p. 47. Then

$$L \text{ (in calories)} = -(\text{slope of line} \times 2.303 \times 1.987).$$

In many cases it is more convenient to use a formula obtained by integrating between limits, p_2 at T_2 and p_1 at T_1, as follows:

$$\int_{p_1}^{p_2} d \ln p = \int_{T_1}^{T_2} \frac{L}{R} T^{-2}\, dT$$

$$\ln p_2 - \ln p_1 = \frac{L}{R}\left(-\frac{1}{T_2} - \left(-\frac{1}{T_1}\right)\right)$$

$$\log p_2 - \log p_1 = \frac{1}{2.303}\frac{L}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

$$\log \frac{p_2}{p_1} = \frac{L\,(T_2 - T_1)}{2.303 \times 1.987 \times T_2 \times T_1}. \tag{60}$$

Using this equation it is possible to calculate the heat of vaporization from the vapor pressures at two different temperatures; and if the heat of vaporization and the vapor pressure at one temperature are known, the vapor pressure at any other temperature may be calculated. Any units of pressure and heat may be used as long as L and R are

taken in the same units. This formula is quite satisfactory unless the temperature range is so great that the heat of vaporization can no longer be considered constant.

The unintegrated expression is most convenient in correcting boiling-points for barometric fluctuations. For *small* changes in pressure it may be assumed that the change in boiling-point with pressure is given by the formula

$$\frac{dT}{dp} = \frac{RT^2}{Lp}. \tag{61}$$

Free Energy. It has been shown that a system has a certain content of internal energy, U, and that the decrease of internal energy in changing from one state to another is measured by the heat evolved at constant volume, i.e., by the maximum heat evolved under conditions such that none of the energy can do work. Then $-\Delta U = -q$. In the same way we may consider that a system has a certain work content, A, and that the decrease in work content, $-\Delta A$, during a change is measured by the maximum work which can be done. Then

$$-\Delta A = w_{\max}.$$

As in the case of the internal energy, the value of ΔA depends solely on the initial and final states.

The system may change under conditions such that the work obtained, w, is not equal to $-\Delta A$, as for example when some heat is evolved. However $-\Delta A$ represents the maximum work, $w_{\max}$, which might have been obtained and would be obtained if the change were carried out reversibly.

This maximum work, $-\Delta A$, which can be obtained when a system undergoes a change may be resolved into two parts: one involving pressure-volume work and the other involving electrical and all other forms of work except pressure-volume work done against the atmosphere.

The work involved in the volume change is a necessary accompaniment of the change, but the remainder of the work is available for other purposes and is called the change in free energy and given the symbol ΔF. F bears to A the same relation that H bears to U and is defined as follows: —

$$F = A + pv^*.$$

* This definition of free energy is in agreement with the notation of G. N. Lewis which is adopted in this book. Many authors, including German writers, assign the term " free energy " to the quantity, A, and some confusion exists. The free energy term F is identical with ζ in the notation of Willard Gibbs. There is complete agreement as to the importance of F; the only disagreement lies in the name given to it.

The concept of free energy is most useful under conditions of constant pressure and then

$$\begin{aligned} \Delta F = F_2 - F_1 &= A_2 + p_2 v_2 - (A_1 + p_1 v_1) \\ &= \Delta A + p\,\Delta v = -w_{\max} + p\,\Delta v \end{aligned}$$

and

$$-\Delta F = w_{\max} - p\,\Delta v. \tag{62}$$

If the pressure is not constant it is evident from the rule for differentiating a product that another term must be included and

$$dF = dA + d(pv) = dA + p\,dv + v\,dp \tag{63}$$

and, integrating between limits,

$$\int_{F_1}^{F_2} dF = \int_{A_1}^{A_2} dA + RT\int_{v_1}^{v_2} \frac{dv}{v} + RT\int_{p_1}^{p_2} \frac{dp}{p}. \tag{64}$$

$$F_2 - F_1 = A_2 - A_1 + RT \ln \frac{v_2}{v_1} + RT \ln \frac{p_2}{p_1}. \tag{65}$$

$$\Delta F = \Delta A + RT \ln \frac{v_2}{v_1} + RT \ln \frac{p_2}{p_1} = RT \ln \frac{p_2}{p_1}. \tag{66}$$

All spontaneously occurring processes involve a decrease in free energy and in general

If ΔF is negative the change can occur spontaneously.
If ΔF is positive the change cannot occur spontaneously.
If ΔF is zero the system is in a state of equilibrium.

For example, the free energy of carbon and oxygen is greater than the free energy of carbon dioxide so it is possible for carbon and oxygen to combine and form carbon dioxide. Thermodynamics has nothing to say about time and carbon may exist for a long time in contact with oxygen; but the reaction *is possible*, and it will take place under proper conditions. The reverse process — the decomposition of carbon dioxide — involves an increase in free energy, and it can occur only with the help of some outside agency, or by heating to a very high temperature where the free energy conditions are reversed. Water and ice have the same free energy at 0° and the two are in equilibrium. There is no tendency for ice to melt or water to freeze in a mixture which is at 0°.

A kinetic interpretation is helpful. When water molecules fall they have a vertical motion which can be used in running a turbine, and when electrons from a battery flow along a wire they exert a magnetic field which can be utilized for doing useful work. In general, work can be done when a system passes from one state to another state of

lesser free energy content, provided some kind of ordered motion is involved. If no mechanism is available for converting this ordered motion into work the change will take place, and all the free energy decrease, which might have been utilized in work, is then converted into un-ordered motion of molecules — namely, heat.

The relative amounts of work and heat can be altered at will by changing the conditions and arranging to obtain more or less ordered motion, but the amount of work done during the change cannot exceed $-\Delta A$, and this amount will be realized only in case the change takes place reversibly.

The Gibbs-Helmholtz Equation. The quantitative relationship between maximum work and heat is given by the Gibbs-Helmholtz equation, which is derived from the first and second laws of thermodynamics in the following manner.

According to the second law

$$dw_{\max} = q_{\text{rev}} \frac{dT}{T} \tag{67}$$

and substituting $-d(\Delta A)$ for the infinitesimal quantity of work, $dw_{\max}$, corresponding to the infinitesimal drop in temperature, dT

$$q_{\text{rev}} = -T \frac{d(\Delta A)}{dT}. \tag{68}$$

Applying the first law to the special case of a reversible process

$$q_{\text{rev}} = \Delta U + w_{\max} = \Delta U - \Delta A. \tag{69}$$

Substituting and imposing the restriction of constant volume

$$\Delta A - \Delta U = T\left(\frac{\partial(\Delta A)}{\partial T}\right)_v. \tag{70}$$

At constant pressure, with the help of certain substitutions, and a relation involving entropy (defined on p. 522) it can be shown that

$$\Delta F - \Delta H = T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p. \tag{71}$$

According to this equation the difference between the change in free energy and the heat of reaction at constant pressure is equal to the absolute temperature multiplied by the rate at which free energy increases with the temperature. Examples of this important equation will be given in a later chapter.

The Theorem of Le Chatelier. Earlier attempts to discover a relation between thermodynamics and chemical affinity led Berthelot in 1879 to the false conclusion that the evolution of heat in a chemical

reaction is a measure of chemical affinity. The mere existence of spontaneous reactions which absorb heat and the general reversibility of all reactions show that this conclusion cannot be right. In some cases where there is little change in heat capacity it serves as a very rough approximation.

Another qualitative principle known as the theorem of Le Chatelier has been useful in predicting the direction in which a change may be expected. According to this theorem, if a system is in equilibrium and an external force is applied, the system will shift in such a way as to minimize the effect of the applied force. For example, if pressure is applied to ice, the ice melts to give liquid water which has a smaller volume and the pressure is relieved. Other examples will be given in later chapters.

It must be emphasized that the theorem of Le Chatelier tells nothing that the second law of thermodynamics does not tell; that it is only qualitative in nature and that it is not rigidly true in every case. The concept of free energy is more quantitative and more useful in predicting the direction of change in a physical or chemical system.

REFERENCES

The Fundamentals of Chemical Thermodynamics. Butler.
Thermodynamics and the Free Energy of Chemical Substances. Lewis and Randall.
Thermodynamics for Students of Chemistry. Hinshelwood.
Chemical Thermodynamics. Partington.
Thermodynamics and Chemistry. MacDougall.

PROBLEMS

1. A piston whose diameter is 20 cm. moves 10 cm. under a pressure of 10 atmospheres. How much work is done?

2. A kilogram weight falls 100 meters. (*a*) How many ergs of heat are liberated when it strikes the ground? (*b*) How many joules? (*c*) How many calories? (*d*) How many cc.-atmospheres?

3. Ten grams of aluminum is dissolved in an excess of hydrochloric acid at 25°. Will more heat be evolved when this action is carried out in a closed bomb or in an open beaker? How much more?

4. How many liter-atmospheres and how many calories of work is required to condense a mol of mercury vapor at its boiling-point, 360°, to the liquid state under a constant pressure of 1 atmosphere?

5. One mol of hydrogen is heated from 0° to 100° under a pressure of 1 atmosphere. Calculate (*a*) the increase in heat content, (*b*) the increase in internal energy assuming hydrogen to be a perfect gas. The specific heat of hydrogen at constant pressure is 3.41. *Ans.* (*a*) 687 cal. (*b*) 488 cal.

6. (*a*) Calculate the external work done against the atmosphere when one mol of benzene is vaporized at its boiling-point 80.2°. The heat of vaporization at this

temperature is 95.4 cal. per gram. For the vaporization of one mol calculate (*b*) q; (*c*) ΔH; (*d*) ΔU.

7. A gram of water requires 539 calories of heat for evaporation at 100° C. (*a*) How much heat is required to evaporate a mol? (*b*) How much of this energy is utilized as work in increasing the volume of the system? (*c*) What happens to the rest of the energy which is absorbed?

8. A mol of gas is compressed isothermally and reversibly at 27° from 1 atmosphere to 10 atmospheres. What is the value of w? *Ans.* $w = -56.7$ liter-atmospheres.

9. One liter of gas at 0° C. under 10 atmospheres pressure expands suddenly under one atmosphere pressure to a volume of 10 liters at 0°. How many liter atmospheres of work are done? (*b*) The gas is expanded to 5 liters under 2 atmospheres pressure and then the 5 liters is expanded to 10 liters under 1 atmosphere? How much work is done? (*c*) The gas is expanded to 2 liters under 5 atmospheres pressure, then to 4 liters under $2\frac{1}{2}$ atmospheres pressure, and then to 10 liters under 1 atmosphere pressure. How much work is done? (*d*) The pressure is reduced gradually by infinitesimal amounts till the volume is 10 liters and the pressure 1 atmosphere. How much work is done? (*a*), (*b*) and (*c*) involve isothermal expansions at *constant* pressure.

10. What is the maximum number of calories of work which can be obtained by the expansion of 1000 g. of mercury vapor at 500° from 2 atmospheres to 1 atmosphere?

11. A mol of helium ($C_v = 3.00$ calories per degree) at 0° is compressed suddenly and adiabatically from 44.8 liters (and 0.5 atmosphere) to 22.4 liters. How much will the temperature rise? *Ans.* 160°.

12. A liter of air under pressure at 25° is allowed to expand under adiabatic conditions until the volume is 2 liters. What will the final temperature be? The heat capacity of air at constant volume is 4.9 calories per degree per mol.

13. Compare the thermodynamic efficiency of a steam engine with that of a mercury vapor engine if the boiler of the former operates at 100° and the boiler of the latter operates at 360°, the condenser in each case operating at 30°.

14. One gram of gasoline evolves 11,200 calories of heat on combustion. If used to run a steam engine with the boiler at 105° and the condenser at 25° what is the maximum work in calories which can be obtained? If used in an explosion engine with the temperature in the cylinder at 600° and the exhaust at 100°, what is the maximum work obtainable?

15. *Theoretically* how high could a gallon of gasoline lift an automobile weighing 3000 pounds against the force of gravity assuming the cylinder temperature is 600° and the exhaust 100°? (Density gasoline = 0.8; 1 lb. = 453.6 g.; 1 liter = 0.2642 gallons. Heat of combustion of gasoline = 11,200 calories per gram.)

16. Discuss the advantages and disadvantages of using diphenyl instead of water for an engine. Diphenyl boils at 254.6° and melts at 70.5°.

17. The density of solid phenol is 1.072, and the density of liquid phenol is 1.0561; its heat of fusion is 24.93 calories per gram, and its freezing-point is 41°. Find the change in the freezing-point produced by an increase in pressure of 1 atmosphere.

18. Acetic acid melts at 16.6°, $dT/dp = 0.0242°$ per atmosphere, and the heat of fusion is 46.42 calories per gram. Calculate the change in volume accompanying the liquefaction of 1 g. of acid.

19. The heat of vaporization of ether is 88.39 calories per gram at its boiling-point, 34.5°. (*a*) Calculate the rate of change of vapor-pressure with temperature $\frac{dp}{dT}$. (In formula (55) R is taken in calories to agree with the units in which L is expressed.) (*b*) What is the boiling-point at 750 mm.? (*c*) What is the vapor pressure at 36.0°?

20. At 70° carbon tetrachloride has a vapor pressure of 622.3 and at 80° a vapor pressure of 843.0 mm. Calculate the molar heat of vaporization of carbon tetrachloride using the formulas

(*a*) $\frac{\Delta p}{\Delta T} = \frac{Lp}{RT^2}$ and (*b*) $\log \frac{p_2}{p_1} = \frac{L(T_2 - T_1)}{4.575\, T_2 T_1}$. *Ans.* (*a*) 7250. (*b*) 7300.

21. From the data of the preceding problem (#20) calculate (*a*) the normal boiling-point, i.e., the temperature at which the pressure becomes 760 mm., (*b*) the change in boiling-point per mm. pressure, $\frac{dT}{dp}$, at 760 mm.

22. The vapor pressure of benzene at 10° is 45.3 mm. and at 70° it is 547.4 mm. (*a*) What is the molar heat of vaporization as calculated from the integrated formula? (*b*) What is the relation between this quantity and the slope of the line obtained in Prob. 10 on p. 61?

23. What is the boiling-point of water at Quito, where the average barometer reading is 524.5 mm.? The normal boiling-point at 760 mm. is 100.0° and the heat of vaporization at this temperature is 539 calories per gram. *Ans.* 89.7°.

24. A certain liquid boils at 96.90° under 730 mm. pressure and at 97.11° under 740 mm. What is the normal boiling-point at 760 mm.?

25. The normal boiling-point of nitrobenzene is 210° and its heat of vaporization at this temperature is 79.1 calories per gram. Estimate the vapor pressure of nitrobenzene at 25° C.

26. The normal boiling-point of acetone is 56.1° and the heat of vaporization 124.5 calories per gram. What is the boiling-point at a pressure of 750 mm.?

Ans. 55.7°.

27. At 0° ice absorbs 80 calories in melting and water absorbs 597 calories in vaporizing. (*a*) What is the heat of sublimation of ice at this temperature? (*b*) At 0° the vapor pressure of both ice and water is 4.6 mm. What is the rate of change of vapor pressure with temperature $\left(\frac{dp}{dT}\right)$ for ice at this temperature? (*c*) How much greater is it than the corresponding value for liquid water?

28. Point out *all* the approximations involved in the derivation of the Clapeyron equation and the Clausius-Clapeyron equations.

29. A mol of liquid benzene is vaporized at 80.2° under a constant pressure of 1 atmosphere. The vapor can be condensed by an infinitesimal increase in pressure. (*a*) What is the value of ΔA? (*b*) What is the value of ΔF?

Ans. (*a*) −702.1 cal. (*b*) 0.

30. What is the value of ΔA and ΔF for the isothermal reversible condensation of 1 mol of mercury vapor at 360° under 1 atmosphere pressure?

CHAPTER VII

SOLUTIONS

Definition of Terms. Having dealt with the properties of pure substances in the gaseous, liquid and solid states we now proceed to the consideration of the properties of mixtures of two or more pure substances. When such a mixture is chemically and physically homogeneous it is termed a *solution.*

A solution may also be defined as a homogeneous phase composed of two or more chemical substances. Thus, when alcohol is added to water, we obtain, when equilibrium has been established, a homogeneous, single-phase system composed of two different chemical substances uniformly and intimately mixed with each other. Such a system constitutes a true solution as distinguished from so-called colloidal solutions, which will be discussed in a subsequent chapter.

When one substance is dissolved, or molecularly dispersed, in another, it is customary to designate as the *solvent* that component which is present in the larger proportion, and to call the other component the *solute.* It should be remembered that this method of designation is purely arbitrary, and that the ability of one substance to dissolve in another does not imply that one component possesses greater solvent power than the other. In fact, it frequently happens that two liquids are miscible in all proportions, in which case either one may be regarded as the solvent. Such liquids are said to be *consolute.*

While no general principle has as yet been discovered by means of which the solubility of one substance in another can be predicted, it is nevertheless true that solubility is to a large extent dependent upon the existence of a similarity in character between the components of a solution. For example, benzene is insoluble in water but mixes in all proportions with its homologue, toluene. Likewise, a great number of organic compounds, such as the solid hydrocarbons and fats, which are insoluble in water, dissolve readily in ether or benzene. On the other hand, numerous inorganic salts dissolve in water over a wide range of concentration, notwithstanding the fact that they bear little or no resemblance to the solvent.

Modes of Expressing the Composition of Solutions. There are several different ways in which the composition of a solution may be expressed. Each has advantages for particular purposes.

Volume concentrations are used in volumetric analysis because it is convenient to introduce with each cubic centimeter of solution a definite number of molecules. A *molar solution* (or formal solution) contains 1 mol of solute in a liter of solution. A *normal solution* contains an equivalent weight (i.e., molecular weight divided by the valence) in a liter of solution, but it is necessary to specify whether the solution is normal with respect to neutralization or oxidation or other reaction.

Weight concentrations are used in scientific work because they are uninfluenced by temperature, whereas the volume concentrations are subject to variations caused by changes in density. *A molal solution* contains 1 mol of solute dissolved in 1000 grams of solvent. The term "molal" usually refers to weight concentrations whereas the term "molar" usually refers to volume concentrations. One may be converted into the other when the density of the solution is known.

Mol fractions are used in theoretical work because many physical properties of solutions are expressed most simply in terms of the relative numbers of molecules. The mol fraction of a dissolved substance is defined as the number of mols of the substance divided by the total number of mols. Thus, if a solution is composed of n_A mols of A and n_B mols of B, the mol fractions of the two components will be as follows:

$$\text{mol fraction of } A = N_A = \frac{n_A}{n_A + n_B}.$$

$$\text{mol fraction of } B = N_B = \frac{n_B}{n_A + n_B}.$$

It is obvious that the mol fraction of A plus the mol fraction of B must be equal to 1. If three or more different substances are involved, the denominator in each case contains the total number of mols of all kinds.

Percentage by weight is often used in technical work to express the concentration of a solution.

These four different methods may be illustrated with a solution containing 1 mol of ethanol (46 grams) in 1000 grams of water, the density of which is 0.992.

Weight Concentration.

$$\frac{1 \text{ mol}}{1000 \text{ g.}} = 1 \text{ molal.}$$

Volume Concentration.

$$\frac{1 \text{ mol}}{\frac{1000 + 46}{0.992} \text{ cc.}} \times 1000 = 0.948 \text{ molar.}$$

Mol Fractions.

$$N_1 = \frac{\frac{1000}{18}}{\frac{1000}{18} + \frac{46}{46}} = 0.982.$$

$$N_2 = \frac{1}{\frac{1000}{18} + 1} = 0.0177.$$

Percentage by Weight.

$$\text{Percentage } H_2O = \frac{1000}{1046} \times 100 = 95.6.$$

$$\text{Percentage } C_2H_5OH = \frac{46}{1046} \times 100 = 4.4.$$

Classification of Solutions. There are nine possible classes of solutions, as follows: —

(1) Solution of gas in gas;
(2) Solution of liquid in gas;
(3) Solution of solid in gas;
(4) Solution of gas in liquid;
(5) Solution of liquid in liquid (liquid pairs);
(6) Solution of solid in liquid;
(7) Solution of gas in solid;
(8) Solution of liquid in solid;
(9) Solution of solid in solid.

Although examples of all of these different types of solutions are known, only the more important classes will be considered here.

Solutions of Gases in Gases. In solutions of this class, the components may be present in any proportions, since gases are completely miscible. In a mixture of gases where no chemical action occurs, each gas behaves independently, the properties of the gaseous mixture being the sum of the properties of the constituents. Thus, *the total pressure of a mixture of several gases is equal to the sum of the pressures which each gas would exert were it alone present in the volume occupied by the mixture.* This law was discovered by Dalton and is known as *Dalton's law of partial pressures.* If the partial pressures of the constituent gases be denoted by p_1, p_2, p_3, etc., and P and V represent the total pressure and the total volume of the gaseous mixture, then

$$PV = V(p_1 + p_2 + p_3 + \ldots). \qquad (1)$$

Dalton's law holds when the partial pressures are not too great, its order of validity being the same as that of the other gas laws. Dalton's

law can be tested experimentally by comparing the total pressure of the gases with the sum of the pressures exerted by each gas before mixture. The possibility of measuring the partial pressure of one of the two components of a gas mixture, provided a diaphragm could be found which would be pervious to one of the gases but not to the other, was first pointed out by van't Hoff. It was shown by Ramsay * that the walls of a vessel of palladium, when sufficiently heated, permit the free passage of hydrogen but not of nitrogen. The walls are said to be *semi-permeable*. A sketch of the apparatus used by Ramsay in the verification of Dalton's law is shown in Fig. 52. A small vessel of palladium P, containing nitrogen, is connected with a manometer AB which serves to measure the pressure of the gas in P. The vessel P is enclosed within a larger vessel C, which is filled with hydrogen at a known pressure. On heating P and passing a current of hydrogen at a definite pressure through C, the hydrogen enters P until the pressures due to hydrogen inside and outside are equal. The total pressure in P, measured on the manometer, increases until it is practically equal to the pressure of hydrogen in C plus the original pressure of the nitrogen.

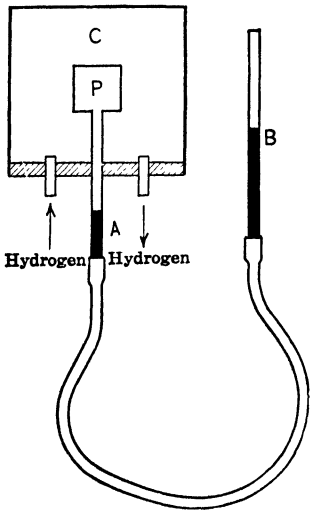


FIG. 52

Solutions of Gases in Liquids. The solubility of gases in liquids is limited, the extent to which they dissolve depending upon the pressure, the temperature, the nature of the gas, and the nature of the solvent. When a liquid cannot absorb any more of a gas under equilibrium conditions at a definite temperature, it is said to be *saturated*, and the solution is called a *saturated solution*.

The number of gas molecules entering a liquid at its surface is proportional to the concentration of the molecules in the gas phase, c_2, and the number leaving the liquid is proportional to the concentration of the dissolved gas, c_1, in the liquid. Then at equilibrium in a saturated solution the rate of escape of dissolved molecules from the liquid into the gas phase is equal to the rate at which molecules dissolve in the liquid from the gas phase and

$$k_1 c_1 = k_2 c_2 \qquad (2)$$

* Phil. Mag. (5), **38**, 206 (1894).

where k_1 and k_2 are proportionality constants.

Then
$$\frac{c_1}{c_2} = \frac{k_2}{k_1} = K = \text{a constant.} \tag{3}$$

This important relation is known as *Henry's law;* according to it the concentration of the dissolved gas in solution is directly proportional to the concentration in the free space above the liquid. The concentration in the gas phase is usually expressed in terms of pressure, and Henry's law may be written

$$\frac{c}{p} = K. \tag{4}$$

K is called the solubility coefficient; it is defined as the ratio of concentration of dissolved gas, c, to the pressure of the gas, p.

For example, if 0.002 mol of a gas is dissolved in 1000 grams of water under 1 atmosphere pressure, 0.004 mol will be dissolved when the pressure is doubled. Since the volume of a given weight of gas is inversely proportional to the applied pressure and the quantity dissolved is directly proportional to the pressure, it is evident that the volume of a gas dissolved by a liquid is independent of the pressure.

Henry's law, like most of the laws of solutions, is not exact except in very dilute solutions. Up to a pressure of 1 atmosphere it holds within 1 to 3 per cent with many gases. Large deviations are to be expected when the dissolved gas undergoes a secondary reaction with the solvent, as for example when ammonia gas is dissolved in water. Henry's law applies only to the dissolved NH_3, but the concentration in the solution is determined by analytical methods which include both the NH_3 and the NH_4OH formed.

The solubilities of a few gases in water and alcohol as determined by Bunsen are given in the following table. The numbers represent liters of gas reduced to 0° and 760 mm. which dissolve in 1 liter of solvent at 1 atmosphere pressure.

SOLUBILITY OF GASES

Gas	Water		Ethyl Alcohol	
	0°	15°	0°	15°
Hydrogen	0.0215	0.0190	0.0693	0.0673
Oxygen	0.0489	0.0342	0.2337	0.2232
Carbon dioxide	1.797	1.002	4.44	3.28

Dalton showed that the solubility of the individual gases in a mixture of gases is directly proportional to their partial pressures, the solubility of each gas being nearly independent of the presence of the others. The solubility of oxygen in water is nearly twice as great as the solubility of nitrogen, and since the solubility of one gas is unaffected by the presence of the other, the dissolved air is considerably richer in oxygen than the air above water.

The solubility of gases in water is appreciably diminished, however, by the presence of dissolved solids or liquids, especially electrolytes. This "salting out" effect, according to Philip,* is caused by the hydration of the dissolved salt. A portion of water in the solution is supposed to be combined with the salt, and the water which is thus removed from the rôle of solvent is no longer free to absorb gas. The extent of the "salting out" effect varies considerably with different salts, but with a given salt the relative decrease in solubility is the same for different gases. For example, if a certain salt reduces the solubility of oxygen to 80 per cent of its value, the solubility of nitrogen also will be reduced to about 80 per cent of its value. Such a relation is to be expected if the salt merely reduces the amount of solvent water.

The solubility of a gas in a liquid usually diminishes with an increase in temperature, although there are frequent exceptions. The rate of escape from the liquid is increased more by a rise in temperature than is the rate at which molecules in the gas phase strike the surface and dissolve in the liquid. It is a common observation that a glass of cold water allowed to warm up to room temperature shows the presence of many small air bubbles.

In some cases, as when ammonia is dissolved in water, the deviations from Henry's law become less at high temperatures because the chemical combination with the solvent is less.

With regard to the connection between the solvent power of a liquid and its nature, but little is known. About all that can be said is that the order of solubility of gases in different liquids is almost always the same. Thus in the preceding table the solubilities of hydrogen, oxygen and carbon dioxide in water and in alcohol will be seen to be approximately proportional. A slight change in volume always results when a gas is dissolved in a liquid. In general, it may be said that the less compressible a gas is, the greater is the increase in volume produced when it is absorbed by a liquid. It is of interest to note that the increase in volume caused by the solution of a mol of gas is nearly equal to the corresponding value of b in the equation of van der Waals.

* Trans. Faraday Soc., **3**, 140 (1907).

Liquid Pairs. Solutions of liquids in liquids can be divided into three classes as follows: — (1) Liquids which are miscible in all proportions; (2) liquids which are partially miscible; and (3) liquids which are immiscible. Examples of these three classes in the order mentioned are, alcohol and water, ether and water, and benzene and water. As to the cause of the miscibility and non-miscibility of liquids very little is known.

If a small amount of ether is added to a large volume of water in a separatory funnel and the mixture vigorously shaken, a perfectly homogeneous solution will be obtained. On gradually increasing the amount of ether, shaking after each addition, a concentration will

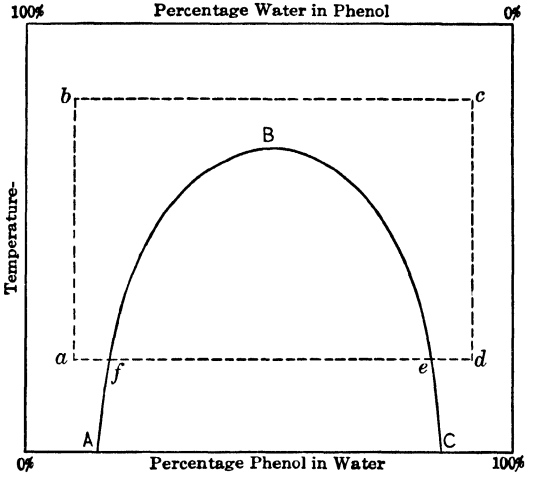


FIG. 53

eventually be reached at which a separation into two layers will take place. The upper layer is a saturated solution of water in ether, and the lower layer is a saturated solution of ether in water. So long as the relative amounts of the two liquids are such that the mixture does not become homogeneous on standing, the composition of the two layers will be independent of the relative amounts of the two components. Measurements of the mutual solubility of liquids have been made by Alexejeff* by placing weighed amounts of two different liquids in sealed tubes and observing the temperature at which the mixture became homogeneous. In general the solubility of a pair of partially miscible liquids increases with the temperature, and therefore it may be inferred that at a sufficiently high temperature any mixture will become

* J. prakt. Chem., **133**, 518 (1882).

perfectly homogeneous. An example of this type of binary mixture is furnished by phenol and water, the solubility curve of which is shown in Fig. 53. In this diagram temperature is plotted on the axis of ordinates and percentage composition of the solution on the axis of abscissas. Starting with a small amount of phenol and adding it in increasing quantities to a large volume of water, a concentration will eventually be reached at which the solution will separate into two layers. This concentration is represented by the point *A*. On raising the temperature, the solubility of phenol in water increases, as shown by the curve *AB*. In like manner, starting with pure phenol and adding increasing amounts of water, separation into two layers will occur at a concentration represented by the point *C*. As the temperature is raised, the solubility of water in phenol increases, as shown by the curve *CB*. When the temperature is raised above 68.4° C., corresponding to the point *B*, phenol and water become miscible in all proportions.

If we start with a solution whose temperature and composition are represented by the point *a*, the addition of increasing amounts of phenol at constant temperature will be represented by the dotted line *afed*. When the point *f* is reached, the solution will separate into two layers the composition of which will be independent of the relative amounts of phenol and water. At *e* the solution will again become homogeneous.

All solutions with compositions between those of *f* and *e*, when cooled to the temperature of this dotted line, will produce two solutions — a solution of phenol saturated with water and a solution of water saturated with phenol. A composition falling midway between *e* and *f* will give equal amounts of the two immiscible solutions, and a composition lying nearer to *f* than to *e* will have more of the solution corresponding to *f*, but the composition of each phase will be the same as before. The ratio of the amounts of each phase is the same as the ratio of the distances along the concentration axis from the specified concentration to *e* and to *f*.

If the solution represented by the point *a* is again chosen as the starting point, and its composition is kept unaltered while the temperature is raised to a value above 68.4° C., the change will be represented by the dotted line *ab*. If now the temperature is maintained constant and the percentage of phenol increased, the alteration in composition will be effected without discontinuity, as represented by the dotted line *bc*. On cooling the solution represented by the point *c* to the initial temperature of *a*, the point *d* will be reached. Thus it is possible to pass from *a* to *d* by the path *abcd* without causing a separation of the components into two layers. There is an analogy between the solu-

bility curve of a pair of partially miscible liquids and the dotted, parabolic curve in the diagram of the isothermals of carbon dioxide, shown in Fig. 7. In both cases there is but one phase outside of the curves, while two phases are coexistent within the area enclosed by the curves. The analogy may be traced further, since in each case only one phase can exist above a certain temperature. The temperature corresponding to the apex of the parabolic curve in Fig. 7 is termed the critical temperature of carbon dioxide, and by analogy the temperature corresponding to the point B in Fig. 53 is called the *critical solution temperature.*

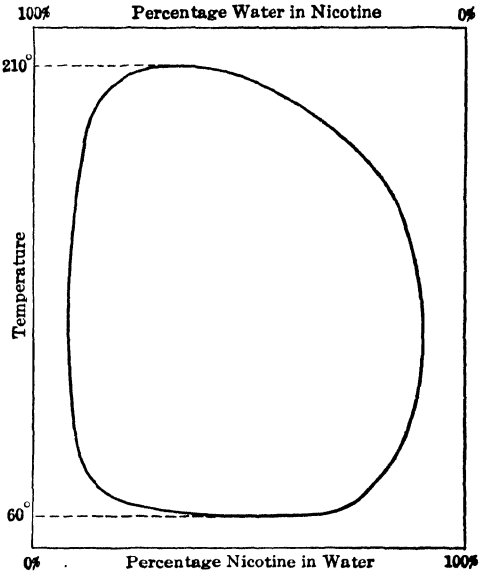


FIG. 54

The mutual solubilities of some pairs of partially miscible liquids were found by Alexejeff to diminish with increasing temperature. Thus, a mixture of ether and water, which is perfectly homogeneous at ordinary temperatures, becomes turbid on warming. A specially interesting pair of liquids is nicotine and water. At ordinary temperatures these liquids are miscible in all proportions. If the temperature is raised above 60° C., and if the composition is within a certain range, the solution becomes turbid owing to incomplete miscibility. On continuing to heat the mixture the mutual solubility of the liquids begins to increase, until at 210° C. they become completely soluble again. The solubility relations of this binary mixture are shown in Fig. 54. The closed solubility curve defines the limits of the coexistence of two layers, all points outside of the curve representing homogeneous solutions.

Ideal Solutions. Henry's Law. It has been shown that an ideal gas is one in which there is no attraction between the molecules and no change in internal energy when the volume is changed. In the same way an ideal solution is one in which no special force of attraction exists between the components of the solution and no change in internal energy is produced on mixing. Under these conditions no

change in the nature of liquids is produced by mixing, merely a dilution of one liquid by the other. When two liquids are mixed to give an ideal solution, there is no heat effect and the properties are strictly additive. The volume of the solution is the sum of the volumes of the two liquids, and there is no more shrinkage or expansion than when two different samples of the same liquid are mixed. Other physical properties of the solution, such as refractive index, fluidity, and vapor pressure, can be calculated directly by averaging the properties of the components which make up the solution.

The vapor pressure of a liquid depends on the rate of escape of molecules from the surface of the liquid, and if the liquid is mixed with another liquid, its concentration in the surface is decreased and its rate of escape diminished. Moreover, in an ideal solution, where the nature of the liquid remains unchanged, the partial vapor pressure of one component is directly proportional to the number of molecules of that component in the mixture. In other words

$$p_A = \frac{n_A}{n_A + n_B}(p_A)_0 = x_A(p_A)_0 \tag{5}$$

where p_A is the partial pressure of the component A, $(p_A)_0$ is the vapor pressure of the pure substance, and $n_A/(n_A + n_B)$ or x_A is the mol fraction of the component A. This important relation is known as *Henry's law*. It will be remembered that this law has already been used to show that the solubility of a dissolved gas is proportional to the pressure of the gas (p. 141).

Ideal solutions are very rare. Only in the case of mixtures whose components are closely related, chemically, will the properties remain unchanged on mixing. Benzene and toluene give a solution which is nearly ideal as seen by the accompanying table due to Schmidt.* The total pressure at different mol fractions is given in the second column. The partial pressures of toluene and benzene are given in the next two columns as calculated from Henry's law and the vapor pressures of the pure liquids. The sum of the two calculated pressures given in the last column checks well with the experimentally determined pressures, but even with these closely related substances the solution is not ideal over the whole range of concentrations. The slight deviations are in agreement with the fact that a slight cooling effect is observed when the two liquids are mixed.

In general, the lack of agreement between the observed and calculated values of the vapor pressures of binary liquid mixtures is much

* Z. phys. Chem., **99**, 80 (1921).

VAPOR PRESSURES OF MIXTURES OF BENZENE AND TOLUENE AT 20°

Mol Fraction Benzene	Total Press. Obs.	Partial Press. Toluene	Partial Press. Benzene	Total Press. Calc.
0.0	24.5	24 5	.....	.....
0.1	30 0	22.1	7.7	29.8
0.2	36 0	19 6	15.3	34.9
0.3	41.5	17.2	23.0	40.2
0.4	47.0	14 7	30.6	45.3
0.5	51.0	12 2	38.2	50.4
0.6	56 0	9 8	45 9	55.7
0.7	62 0	7.3	53 5	60.8
0.8	67.5	5.1	61.2	66.3
0.9	74 0	2.4	68.8	71.2
1.0	76.5	.....	76.5	76.5

greater than in the case of mixtures of benzene and toluene. The following table, also due to Schmidt, gives the vapor pressures of mixtures of benzene and methyl alcohol, two liquids of widely divergent character.

VAPOR PRESSURES OF MIXTURES OF BENZENE AND METHYL ALCOHOL AT 20°

Mol Fraction Methyl Alcohol	Total Press. Obs.	Partial Press. Benzene	Partial Press. Methyl Alcohol Calc.	Total Press. Calc.
0.0	76.5	76.5	.....	76.5
0.1	106 5	68.9	9.4	78.3
0.2	128 0	61.2	18.8	80.0
0.3	139 5	53.6	28.2	81.8
0.4	144.0	45.9	37.6	83.5
0.5	145 5	38.3	47.0	85.3
0.6	145.0	30.6	56.4	87.0
0.7	145.0	23.0	65.8	88.8
0.8	141.5	15 3	75.8	91.1
0.9	123.0	7.7	84.6	92.3
1.0	94.0	.....	94.0	94.0

Vapor Pressure of Binary Mixtures. The study of the vapor pressures of binary mixtures of completely miscible liquids is of great importance in connection with the separation of the liquids by distillation.

The experimental investigations of Konowalow* on homogeneous binary mixtures of liquids have shown that they may be divided into three classes as follows:

(1) Mixtures having vapor pressures intermediate between the vapor pressures of the pure components, e.g., methyl alcohol and water; (2) mixtures having a minimum vapor pressure corresponding to a definite composition, e.g., formic acid and water; and (3) mixtures having a maximum vapor pressure corresponding to a definite composition, e.g., propyl alcohol and water.

In considering the possibility of separating binary liquid mixtures belonging to any one of these three classes, it is essential to determine the composition of both liquid and vapor phases. When a pure liquid is boiled the composition of the escaping vapor is the same as that of the liquid itself, but this is true only for ideal solutions or for ordinary mixtures under special conditions.

A diagrammatic representation of the vapor pressures, at a single temperature, of all possible mixtures of two liquids A and B belonging to Class (1) are given in Fig. 55. Since the vapor pressure can be expressed in terms of the composition of either the liquid or the vapor phase, it follows that there should always be two curves in such a diagram, one referring to the liquid and the other to the vapor phase. In Fig. 55 the curves $Al'lB$ and $Avv'B$, represent the variation in the vapor pressure of the liquid and vapor phases, respectively, with change in composition.

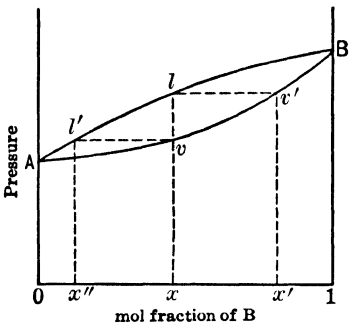


FIG. 55

Since the vapor is relatively richer in the more volatile component, it follows that the curve representing vapor composition must always lie closer to the component which has the higher vapor pressure. In Fig. 55, for example, the curve $Avv'B$ must lie nearer to the ordinate corresponding to pure B than the curve $Bll'A$. By determining where a horizontal line cuts the two curves, we can ascertain the equilibrium concentrations of the two phases. Thus, if x denotes the mol fraction of B in the liquid phase, x' will be the equilibrium concentration of B in the vapor phase: or, if x denotes the concentration of B in the vapor phase, x'' will be the equilibrium concentration in the liquid phase.

In other words, if a binary liquid mixture having the composition x is subjected to a process of isothermal distillation, we shall at first

* Wied. Ann., **14**, 34 (1881).

obtain a vapor whose composition is x'. As the evaporation proceeds, however, the composition of the liquid phase will become less rich in the component B, and assuming that it is in equilibrium with the vapor, the last drop of liquid to evaporate will have the composition represented by x'' while the corresponding composition of the vapor phase will be represented by x. Mixtures of this class can be separated into their components by fractional distillation.

Similar vapor pressure diagrams corresponding to the other two classes of binary liquid mixtures are given in Figs. 56 and 57.

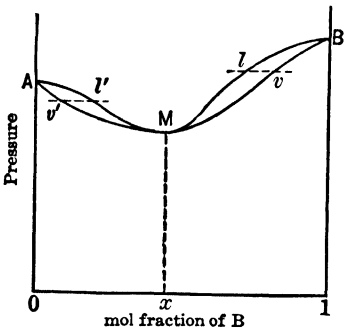


FIG. 56

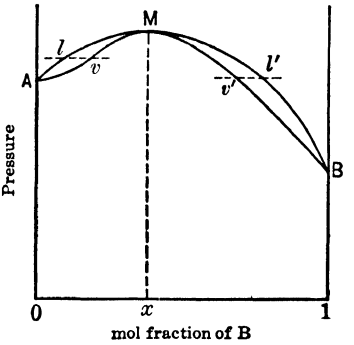


FIG. 57

Distillation of Binary Mixtures. In the preceding paragraphs we have seen that the vapor-pressure curves of binary liquid mixtures at constant temperature may be divided into three classes. Similarly, when such mixtures are distilled under constant pressure, we also distinguish three corresponding classes of boiling-point curves.

In Class (1) the boiling-points of all possible mixtures are intermediate between those of the two components. All mixtures belonging to Class (2) exhibit a maximum in their boiling-point curves corresponding to a minimum in the vapor-pressure curve, while the mixtures of Class (3) exhibit a minimum. Each of these three classes of curves is illustrated diagrammatically in Figs 58 to 60. Since, in binary liquid mixtures, the lower-boiling component, i.e., the component with the higher vapor pressure is present in relatively greater amount in the vapor phase, it follows that, in each of the three diagrams, the upper curve corresponds to the vapor phase.

Let x, Fig. 58, represent the composition of a liquid mixture belonging to Class (1). When this mixture is distilled, the first portion of vapor to condense will have the composition x' and, as distillation proceeds, the liquid phase will become gradually poorer in the component B. The vapor phase being removed by condensation, the boiling-

point will continue to rise until the liquid remaining in the distilling flask is pure A.

Any binary mixture of this class can be more or less completely separated into its components by the process of *fractional distillation.*

For example, if x represents the composition of a large quantity of liquid at l, x' represents the composition of the first vapor, v, to be distilled and if this vapor is condensed by cooling to l' and again distilled, the vapor, v', will now have the composition represented by x''. In other words, by the process of fractional distillation the concentration of the more volatile component, B, has been increased in the distillate and correspondingly decreased in the residue. By continuing the process of successive condensation and distillation it is possible to obtain pure B in the distillate and pure A in the residue. In practice each successive distillation involves an appreciable change in concentration and the average concentration must be considered.

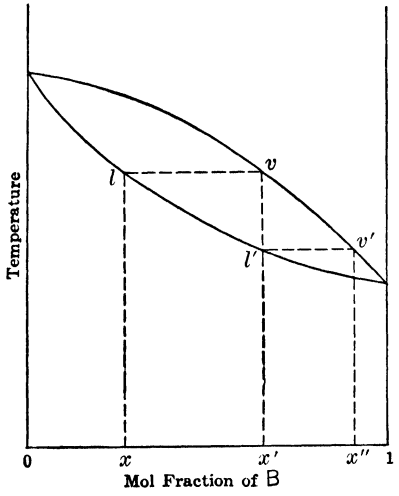


FIG. 58

Binary mixtures of Class (2) exhibit a maximum in their boiling-point curves, as shown at M in Fig. 59. On distilling a mixture whose initial composition corresponds to l, the liquid phase will become relatively richer in the component B, and the boiling-point will continue to rise until, ultimately, if the vapor be allowed to condense, the liquid phase will acquire the composition corresponding to M. This being a constant-boiling mixture, it will behave in many respects like a pure compound, and will distil without change in composition, provided the pressure remains constant. Similarly, if a mixture whose initial composition corresponds to l' be distilled, the liquid phase will become relatively richer in the component A, and finally, will acquire the composition of the mixture having the maximum boiling-point. A partial list of

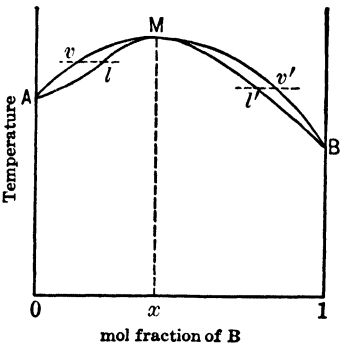


FIG. 59

binary liquid mixtures having constant maximum boiling-points under atmospheric pressure is given in the following table.

BINARY MIXTURES HAVING MAXIMUM BOILING-POINTS

Components	Boiling-Point (Pressure = 760 mm.)	Composition of Mixture at B.-P.
Water + HNO_3	120 5°	68% HNO_3
Water + HCl	110	20 2% HCl
Water + HBr	126	47.5% HBr
Water + HI	127	57 0% HI
Water + HF.	120	37.0% HF
Water + H.COOH	107.1	77.9% H.COOH
$CHCl_3$ + CH_3COCH_3	64.7	80.0% $CHCl_3$

The mixture of hydrochloric acid and water has been studied extensively and the composition of the constant-boiling mixture is so reproducible that it is used as a standard in quantitative analysis. If any solution of hydrochloric acid is boiled for a sufficient time under a pressure of 760 mm. the temperature will gradually rise to 110° and remain stationary, and the mixture boiling at this constant temperature will contain 20.2 per cent hydrochloric acid by weight. From solutions containing less than 20.2 per cent it is possible by continued fractional distillation to recover pure water in the distillate, but it is not possible to recover pure hydrochloric acid. The pure acid may be recovered, however, by fractional distillation of a mixture containing more than 20.2 per cent.

A large number of pairs of liquids are also known whose boiling-point curves pass through a minimum as shown in Fig. 60. These mixtures obviously belong to Class (3). Any mixture whose composition lies between that of A and M, Fig. 60, may be separated more or less completely into pure A and the mixture M by fractional distillation. In this case pure A is left in the residue and mixture M is obtained as the distillate. In like manner, mixtures whose composition lies between that of B and M can also be separated by fractional distillation into pure B and the mixture M. Pure B, however, cannot be obtained on distilling a mixture whose composition lies between that of A and M.

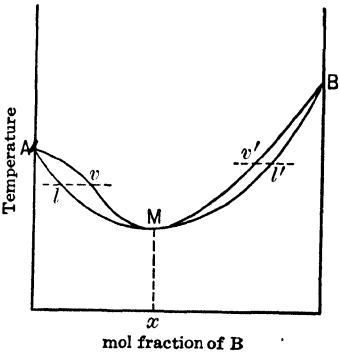


FIG. 60

If the initial composition of a mixture belonging to this class differs but slightly from that corresponding to M, it is apparent from the diagram that the composition of the liquid phase will gradually change as the process of distillation continues. It follows, therefore, that unless great care is taken to prepare a mixture whose composition is exactly the same as that of M, the boiling-point will slowly rise and the composition of the mixture will undergo a gradual change. Ethyl alcohol (b.-p. 78.3°) and water (b.-p. 100°) furnish an interesting example of a pair of liquids belonging to this class of mixtures. The mixture containing 95.57 per cent of alcohol by weight has a minimum boiling-point of 78.13°. Any mixture containing less than 95.57 per cent of alcohol behaves similarly to mixtures of Class (1), and can be completely separated by fractional distillation into pure water and 95.57 per cent ethyl alcohol. Theoretically, it should be possible to fractionate mixtures having compositions lying between 95.57 per cent alcohol and pure alcohol; practically, however, the difference between the boiling-points of the minimum-boiling mixture and that of pure alcohol is so small that the composition of all mixtures within this range changes with extreme slowness.

Maxima and Minima. Maxima and minima are not confined to vapor-pressure and boiling-point curves, but they are sometimes found also when freezing-points, densities, viscosities, specific heats and other properties are plotted against composition. *They are not found in ideal solutions.* Whenever a maximum exists, there must be at least two opposing factors, one tending to increase the magnitude of the property and the other tending to decrease it as the concentration is changed.

In the case of hydrochloric acid and water the minimum in the vapor-pressure curve, or maximum in the boiling-point curve, is due to the ionization of hydrochloric acid. Water and pure hydrochloric acid have high vapor pressures but the hydrogen ions and chloride ions cannot escape from the solution. It will be shown in the next chapter that they lower the vapor pressure of the water. In small amounts, hydrochloric acid added to water lowers the vapor pressure through its ions, but in large amounts, it increases the vapor pressure by adding to the solution the more volatile hydrochloric acid molecules, a fact which can be realized from the sharp odor of hydrochloric acid in the concentrated solutions.

It was thought for a long time that maxima of this type correspond to definite chemical compounds, and such is actually the case in freezing-point curves which will be studied later. The composition of 20.2 per cent HCl in the constant-boiling mixture corresponds very closely to the formula $HCl \cdot 8\ H_2O$ but the relation is accidental.

Roscoe* showed that these mixtures are not definite chemical compounds since the composition of the distillate changes when the distillation is carried out under different pressures. Usually these maxima do not come at compositions corresponding to any chemical formula, and if maxima in two different properties occur in the same mixture, they often occur at different compositions.

Chemical combination between the two liquids is, nevertheless, a factor in many solutions, as is also the breaking down of associated molecules when the environment is changed by dissolving in a different liquid. The process of solution is so complicated that up to the present time no satisfactory quantitative interpretation has been possible.

Vapor Pressure of Immiscible Liquids. We now turn to the consideration of the distillation of binary mixtures composed of partially miscible and immiscible liquids. In general, when two liquids are mixed, each lowers the vapor pressure of the other, so that the vapor pressure of the mixture is less than the sum of the vapor pressures of the components. As has already been pointed out, the composition of the two layers in a binary mixture of partially miscible liquids is independent of the relative amounts of the components present; hence the vapor pressure remains constant so long as two separate layers are present.

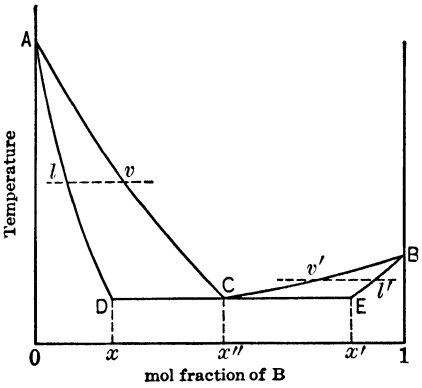


FIG. 61

In general, the boiling-point curves for mixtures of two partially miscible liquids resemble those shown in Fig. 61. Mixtures in which the mol fraction of B lies between 0 and x, and also between x' and 1, consist of a single homogeneous liquid phase. On the other hand, all mixtures whose compositions are included between x and x' consist of two homogeneous liquid phases. If a mixture whose composition corresponds to l is distilled, the initial portions of vapor will have the composition corresponding to v. As distillation proceeds the temperature will rise and the composition of the liquid phase will alter, until eventually nothing but pure A will remain in the distilling flask. In like manner, if a homogeneous mixture whose composition corresponds to l' is distilled, the boiling-point will gradually rise, until that of the pure component B is reached. On the other hand, when any

* Lieb. Ann., **116**, 203 (1860).

mixture whose composition lies between x and x' is distilled, the boiling-point remains constant as long as the two liquid phases are present. The composition of the two phases is represented by x and x' while the composition of the vapor from each phase is represented by x'', this being the composition corresponding to the intersection of the vapor curves, AC and BC. If the process of distillation is continued for a sufficient time, one of the two liquid phases will disappear. If the original two-phase liquid mixture is richer in component A than x'', then the phase represented by x' will disappear, and the boiling-point will increase along DA. Similarly, if the original mixture was richer in component B than x'', the phase represented by x will ultimately disappear, and the boiling-point will increase along EB. Numerous examples of mixtures of this kind are known; of these we may mention water (b.-p. 100°) and isobutyl alcohol (b.-p. 108.4°) which form a two-phase mixture boiling at 88.5°, under a pressure of 760 mm.

The relation between the vapor pressure and the composition of all possible mixtures of a pair of completely immiscible liquids is shown in Fig. 62. When two such liquids are distilled from the same vessel, since neither exerts any influence upon the vapor pressure of the other, the two liquids will continue to distil in the ratio of their respective vapor pressures until one of them is completely vaporized. The straight line, CD, drawn parallel to the axis of composition through the ordinate corresponding to the sum of the vapor pressures of the two components, A and B, represents the relation between vapor pressure and composition. The temperature at which such a system boils will obviously be that at which the sum of the two vapor pressures is equal to that of existing atmospheric pressure.

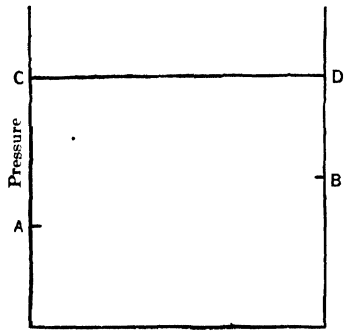


FIG. 62

Since the pressure of a gas is proportional to the number of molecules in a given space, we may express the relation between vapor pressure and composition by the equation:

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} \tag{6}$$

where p_A and p_B are the vapor pressures, and n_A and n_B are the number of mols of A and B. If w_A and w_B denote the weights in grams of A

and B in a known weight of vapor (distillate), and if M_A and M_B are their respective molecular weights, we may write

$$n_A = \frac{w_A}{M_A} \quad \text{and} \quad n_B = \frac{w_B}{M_B}.$$

On substituting these values in equation (6), we have

$$\frac{w_A}{w_B} = \frac{p_A}{p_B} \cdot \frac{M_A}{M_B}. \tag{7}$$

Nitrobenzene and water may be chosen as an example of a pair of liquids which are practically immiscible. Under a pressure of 760 mm. the mixture boils at 99.3° C. The vapor pressure of water at this temperature is 740 mm., and the vapor pressure of nitrobenzene 20 mm. The vapor pressure of nitrobenzene is only 20/740 or one-thirty-seventh as much as the vapor pressure of water, but according to the equation just given the weight of nitrobenzene distilling over is $\frac{20 \times 123}{740 \times 18}$ or nearly one-fifth as much as the weight of water.

If an organic substance is not decomposed by steam, it is possible to effect an appreciable purification by steam distillation, even though its vapor pressure is relatively small. As will be seen from the above example, it is the high molecular weight of the nitrobenzene which compensates for its low vapor pressure. It is the small molecular weight of water which renders it so suitable for distillation of this kind.

Solutions of Solids in Liquids. The solubility of a solid in a liquid is dependent upon the temperature, the nature of the solute and the nature of the solvent. When a solvent has taken up as much of a solute as it is capable of dissolving at a definite temperature, the solution is said to be *saturated*. There are two general methods for the preparation of saturated solutions: — (1) An excess of the finely divided solute is agitated with a known amount of the solvent, at a definite temperature, until equilibrium is attained; or (2) the solvent is heated with an excess of the solute to a temperature higher than that at which saturation is required, and then cooled in contact with the solid solute to the desired temperature. The second method is more rapid but both methods give equally satisfactory results, provided sufficient time is allowed for the establishment of equilibrium, and provided the solid solute is always present in excess.

The solubility of solids has been shown to be somewhat dependent upon their state of division. Thus, Hulett* has found that a saturated solution of gypsum at 25° C. contains 2.080 grams of $CaSO_4$ per liter,

* J. Am. Chem. Soc., **27**, 49 (1905).

whereas when very finely divided gypsum is shaken with this solution, it is possible to increase the content of dissolved $CaSO_4$ to 2.542 grams per liter.

When a saturated solution is cooled, every trace of solid solute being excluded, the excess of dissolved solid may not separate. Such a solution is said to be *supersaturated.*

The explanation of supersaturation is probably to be found in the fact that the submicroscopic crystals which would normally be the first to deposit have a higher solubility and the solution is still unsaturated with respect to them. When an ordinary crystal of the solute with a normal solubility is introduced, however, the extra dissolved material crystallizes out immediately. The greater solubility of the very small crystals may, perhaps, be attributed to the existence of more isolated atoms or groups of molecules which can break away from the crystal more easily. This view is strengthened by the fact that if a mixture of large crystals and very small ones is allowed to stand the small ones disappear and the larger ones grow larger — a procedure which is followed in the digesting of precipitates in quantitative analysis to render them better suited for filtration.

Supersaturated solutions of some substances can be preserved indefinitely, provided all traces of the solid phase are excluded. Such solutions are called *metastable.* On the other hand there are some supersaturated solutions which deposit the excess of solid solute even when all traces of it are excluded. These solutions are termed *labile.* The distinction between metastable and labile solutions is not sharp. If a metastable solution is sufficiently cooled, or if its concentration is sufficiently increased, it may be made to pass over into the labile condition. The concentration at which this transition occurs is termed the *metastable limit.* The stability of supersaturated solutions has been shown by Young* to be greatly influenced by vibrations or sudden shocks within the solution. He has been able to control the amount of overcooling in a supersaturated solution, by altering the intensity of the vibrations due to the friction between glass or metal surfaces within the solution.

The solution of a solid in a liquid is often quite a complicated process. In ideal solutions the molecules break away from the crystal and fill the volume of the solvent until the solution is saturated, in the same way that molecules from a crystal fill an evacuated space. This process absorbs heat corresponding to the heat of sublimation. Ideal solutions are rare and usually the molecules interact with the solvent or undergo ionization and these effects may either absorb or evolve

* J. Am. Chem. Soc., **33**, 148 (1911).

heat. The mere fact that the concentration in solution is usually much greater than the concentration in an evacuated space indicates that the solvent is exerting some special influence on the solute.

The influence of temperature on the solubility depends largely on the total heat effects of the solution as predicted by the principle of Le Chatelier and the second law of thermodynamics. Most salts absorb heat when dissolved and accordingly they are more soluble at the higher temperatures, as in the case of potassium nitrate shown in

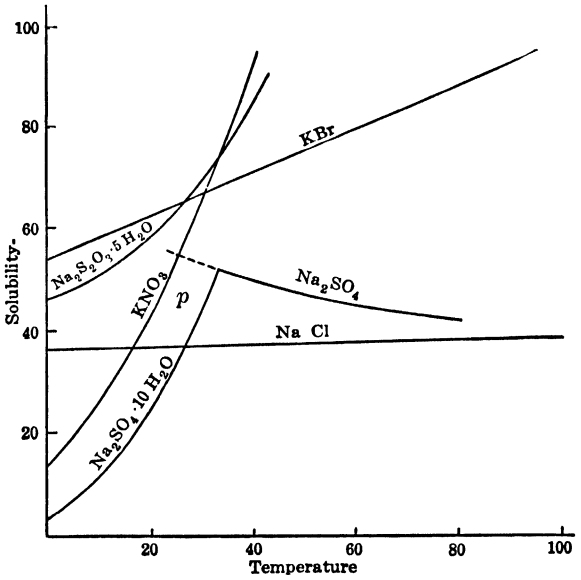


FIG. 63

Fig. 63. If a salt evolves heat on solution, it decreases in solubility as the temperature is raised, as in the case of calcium hydroxide dissolved in water, and sodium sulphate above 40° C. If the different factors are so balanced that heat is neither absorbed nor evolved, as in the case of sodium chloride in water, the solubility is unaffected by temperature. The greater the heat of solution the steeper is the solubility-temperature curve.

Solubility curves are usually continuous except when there is transition from one form to another. One solubility curve shown in Fig. 63 furnishes an illustration. At temperatures below 32.38° the dissolved salt is in equilibrium with the hydrated $Na_2SO_4.10\ H_2O$ which dissolves with the absorption of heat, but at temperatures above 32.38° the dissolved salt is in equilibrium with the anhydrous salt Na_2SO_4 which dissolves with the evolution of heat. Accordingly the solubility of the

hydrated salt increases with temperature, but above the transition temperature the solubility decreases.

That we are actually dealing with two solubility curves is proved by the fact that the solubility curves of the hydrated and anhydrous salts in supersaturated solutions are continuations of the corresponding curves for saturated solutions, as shown by the dotted curve in Fig. 63. If we select any point, such as p, lying between the dotted curve and the full curve, it is apparent that it represents a solution supersaturated with respect to $Na_2SO_4.10\ H_2O$, but unsaturated with respect to Na_2SO_4. If pure anhydrous sodium sulphate is shaken with this solution it will slowly dissolve, whereas if a trace of the hydrated salt is added, the solution will deposit $Na_2SO_4.10\ H_2O$, until the amount remaining in solution corresponds to the solubility of the hydrate at that temperature.

Very little is known concerning the relation between solubility and the specific properties of solute and solvent.

Owing to the fact that the change in volume resulting from the solution of a solid in a liquid is very small, the effect of pressure on the solution is almost negligible. The chief factors conditioning the change in solubility due to increasing pressure are the heat of solution of the solute in the nearly saturated solution, and the change in volume on solidification. Very few experiments have been made to determine the effect of pressure on solubility. It is stated by van't Hoff that the solubility of ammonium chloride, which gives an increased volume on solution, decreases by 1 per cent for 160 atmospheres, while the solubility of copper sulphate, which gives a decreased volume on solution, increases by 3.2 per cent for 60 atmospheres. These data are in agreement with the theorem of Le Chatelier and the second law of thermodynamics.

Solid Solutions. In general, when a dilute solution is sufficiently cooled, the solvent separates in the form of crystals which are almost entirely free from the solute. When, however, the temperature of a solution of iodine in benzene is reduced to the freezing-point, the crystals which separate are found to contain iodine. Furthermore, the depression of the freezing-point of the solvent is found to be less than that calculated on the assumption that the solvent crystallizes uncontaminated with the solute. Such solutions were first studied by van't Hoff.* He found that when the concentration of such abnormal solutions is varied, the ratio of the amount of solute in the liquid solvent to the amount of solute in the solidified solvent remains constant. Thus, in solutions of iodine in benzene, the ratio of the concentration

* Z. physik. Chem., **5**, 322 (1890).

of iodine in the liquid phase to its concentration in the crystallized benzene is constant. In the following table, c_1 is the concentration of iodine in the liquid benzene, and c_2 is the concentration of iodine in the solid benzene.

DISTRIBUTION OF IODINE BETWEEN LIQUID AND SOLID BENZENE

c_1	c_2	c_2/c_1
3.39	1.279	0 377
2.587	0.925	0.358
0.945	0.317	0 336

Since the crystals containing both solute and solvent are perfectly homogeneous, van't Hoff suggested that they be regarded as *solid solutions.*

The mixed crystals which separate from solutions of isomorphous substances, being chemically and physically homogeneous, may also be considered as solid solutions. Many alloys possess the properties characteristic of solid solutions, hardened steel, for example, being regarded as a homogeneous solid solution.

One of the characteristic properties of a dissolved substance is its tendency to diffuse into the pure solvent. Interesting experiments performed by Roberts-Austen* have shown that even solids have the property of mixing by diffusion. Thus, by keeping gold and lead in contact at constant temperature for four years, he was able to detect the presence of gold in the layer of lead at a distance of 7 mm. from the surface of separation. Many other instances of diffusion in solids have been observed.†

Instances of gases and liquids dissolving in solids are also known. Thus platinum, palladium, charcoal and other substances have the property of taking up large volumes of hydrogen. This phenomenon is but little understood. It was suggested by van't Hoff that when hydrogen dissolves in palladium, we are really dealing with two solid solutions, one a solution of hydrogen in palladium, and the other a solution of palladium in solid hydrogen, the system being analogous to that of two partially miscible liquids.

Certain natural silicates, the so-called zeolites, are transparent and homogeneous. Since they contain varying quantities of water they

* Proc. Roy. Soc., **67**, 101 (1900).

† Report on Diffusion in Solids, by C. H. Desch, Chem. News, **106**, 153 (1912).

may be regarded as examples of solutions of liquids in solids. This classification is further justified by the fact that portions of the water may be removed and replaced by other substances, such as alcohol, with apparently no change in the transparency or homogeneity of the mineral.

REFERENCES

Stoichiometry. Young, Chapters XII to XIV.
Solubility. Hildebrand.
The Elements of Fractional Distillation. Robinson.
Distillation Principles and Processes. Young.

PROBLEMS

1. A solution of potassium chloride contains 245.7 g. of salt in 1000 g. of water and the density of the solution at 21° is 1.1310. Calculate the concentration of the solution in (*a*) molality (weight basis), (*b*) molarity (volume basis), (*c*) mol fraction of potassium chloride and mol fraction of water, (*d*) per cent by weight.

2. A solution of nitric acid containing 60.3 per cent nitric acid has a density of 1.375 at 15°. What is the mol fraction of nitric acid? How many mols are contained in a liter of solution? How many mols are contained in 1000 g. of solvent?

3. The density of a 20 per cent aqueous solution of calcium chloride is 1.1753 at 25°. What is the concentration of the solution expressed as mol fractions, as molality (weight basis) and molarity (volume basis)?

4. In a 40 per cent aqueous solution of potassium iodide the densities vary with the temperature as follows:

$t°$	0	20	50	100
d	1.40745	1.39590	1.37548	1.3361

Calculate the molality on the weight basis and the molarity on the volume basis at each temperature.

5. 100 g. of benzene, 50 g. of ethyl alcohol and 200 g. of acetone are mixed together. What is the mol fraction of each?

6. At 550° and 1 atmosphere total pressure the weight of a liter of partially dissociated phosgene is 0.852 g. Phosgene dissociates according to the reaction, $COCl_2 \rightleftarrows CO + Cl_2$. Calculate the degree of dissociation (Chapter II) and the mol fraction of each of the three substances present.

7. 2.3 liters of hydrogen under a pressure of 780 mm. of mercury and 5.4 liters of nitrogen at a pressure of 460 mm. were introduced into a vessel containing 3.8 liters of carbon dioxide under a pressure of 27 cm. What was the total pressure of the mixture?

8. 1.0 g. water and 1.0 g. benzene are evaporated in an evacuated vessel of 5 liters capacity and heated to 200°. What is the pressure of the mixture in atmospheres?

9. At 15°, 1 volume of water absorbs 0.0299 volume of oxygen under atmospheric pressure; and 0.0148 volume of nitrogen under atmospheric pressure. When air (20.9 per cent oxygen and 79.1 per cent nitrogen by volume) is dissolved in water under atmospheric pressure what is the composition of the dissolved air?

Ans. 34.8 mol per cent O_2. 65.2 mol per cent N_2.

10. The dissolved air described in the preceding problem is expelled by boiling into an evacuated space. When this mixture of 34.8 per cent oxygen and 65.2 per cent

nitrogen by volume is dissolved in a very small amount of water under atmospheric pressure, what is the composition of the dissolved gases?

11. At 22°, 100 cc. water dissolves 82.9 cc. of carbon dioxide when the total pressure on the carbon dioxide is 760 mm. Calculate the solubility coefficient and determine the mol fractions present in a solution of carbon dioxide when the pressure is 200 mm. *Ans.* Mol fraction $CO_2 = 0.000162$.

12. Benzene and toluene form a solution which is nearly ideal. At 20° the vapor pressure of the benzene is 76.5 mm. and the vapor pressure of toluene is 24.5. What are the partial pressures and the total pressure of a solution containing 100 g. of each?

13. Ethanol and methanol form a solution which is nearly ideal. Calculate at 25° the partial pressures and the total vapor pressure of a solution obtained by mixing equal proportions by weight. The vapor pressure of ethanol is 59.4 mm. and that of methanol is 150.0 mm.

14. The vapor pressures of benzene and carbon disulphide at 20°, 40°, and 80° are as follows:

	20°	40°	80°
C_6H_6.....	76.5 mm.	185 mm.	755 mm.
CS_2.....	297	617	2030

Calculate the total vapor pressure at each of the above temperatures for a mixture containing one mol of benzene in one mol of carbon disulphide. The observed values of the total pressure at the above temperatures are respectively as follows: 206 mm., 432 mm., and 1475 mm. Calculate the per cent error for each temperature. Is the solution more nearly ideal in its behavior at the highest or lowest temperature?

15. At 35.17° the vapor pressure of chloroform is 293.1 mm. and that of acetone is 344.5 mm. For a solution containing 0.4232 mol fraction of chloroform, calculate the total vapor pressure assuming an ideal solution. The solution is not ideal as shown by the fact that the observed value is 263.2 mm. *Ans.* 322.8 mm.

16. The boiling-point of the immiscible liquid system, naphthalene-water, is 98° C. under a pressure of 733 mm. The vapor pressure of water at 98° C. is 707 mm. Calculate the proportion of naphthalene in the distillate.

17. The vapor pressure of the immiscible liquid system, aniline-water, is 760 mm. at 98° C. The vapor pressure of water at that temperature is 707 mm. How many grams of steam is necessary to distill over 1000 g. of aniline?

18. Solids as well as liquids may be distilled with steam. A mixture of camphor, $C_{10}H_{16}O$, and water boils at 99.3° at 760 mm. pressure. What weight of steam is necessary to purify 200 g. of camphor by steam distillation? The vapor pressure of water at 99.3° is 741.2 mm. *Ans.* 933 g.

CHAPTER VIII

DILUTE SOLUTIONS AND OSMOTIC PRESSURE

Lowering of Vapor Pressure. The lowering of the vapor pressure of a solvent by the addition of a non-volatile solute is responsible for the existence of many relationships of theoretical and practical importance. Because the vapor pressure is lowered, the boiling-point is raised, and the freezing-point is depressed. The phenomenon of osmosis also may be explained as involving the lowered vapor pressure of a solution. All four of these properties are interrelated and they are used for calculating molecular weights and other properties of dissolved substances.

From a kinetic point of view the lowering of the vapor pressure may be explained as due to solute molecules holding back the solvent. The solvent molecules cannot escape so readily when part of the liquid surface is occupied by other molecules and the vapor pressure is therefore lowered.

Raoult's Law. The fundamental law governing the vapor pressure of dilute solutions was established in 1887 by Raoult through exhaustive experimental investigations following the earlier work of von Babo and Wüllner. According to Raoult's law, *the ratio of the lowering of the vapor pressure to the vapor pressure of the pure solvent is equal to the ratio of the number of mols of solute to the total number of mols.* Letting p_0 and p denote the vapor pressures of the solvent and solution, Raoult's law may be formulated thus,

$$\frac{p_0 - p}{p_0} = \frac{n}{N + n} = x \tag{1}$$

where n and N represent the number of mols of solute and solvent, respectively, and x is the mol fraction of the solute. After multiplying out, combining terms, and setting y equal to the mol fraction of the solvent, the law may be written in the form

$$p = p_0 \frac{N}{n + N} = p_0 y \tag{2}$$

from which it is seen that the vapor pressure of a solution containing a non-volatile solute is equal to the vapor pressure of the pure solvent multiplied by its mol fraction in the solution.

Raoult's law applies to the solvent and Henry's law to the solute,

and there is a close relation, as is seen from the following statements (p. 146).

$$\left.\begin{array}{l}\text{Raoult's law.} \quad p_{\text{solvent}} = p_0 \times \text{mol fraction of solvent} = p_0 y \\ \text{Henry's law.} \quad p_{\text{solute}} = k \times \text{mol fraction of solute} = kx,\end{array}\right\} \quad (3)$$

where p is the partial vapor pressure, x the mol fraction of solute and y the mol fraction of solvent, and p_0 the vapor pressure of the pure solvent; k is a proportionality factor which must be determined for each solution. In ideal solutions, Henry's law and Raoult's law become identical because there is then no distinction between solute and solvent and the vapor pressure of each component is equal to the vapor pressure of the pure component multiplied by its mol fraction. In other words, the k in Henry's law becomes the vapor pressure of the pure solute in ideal solutions. But in many real solutions the solute is so changed by contact with the solvent that this relation no longer holds and k must be determined by experiment.

Raoult's law applies to the solvent, which, in dilute solutions, is practically the same as the pure solvent. It is one of the more exact laws of physical chemistry. Both laws hold accurately in ideal solutions at all concentrations and both hold in dilute solutions, but neither holds accurately in non-ideal, concentrated solutions.

The following table* gives experimental data illustrating Raoult's law; the vapor pressure of ethereal solutions was observed at 15°, at which temperature the vapor pressure of pure ether is 360.7 mm.

Solute	Mol. Wt.	Mol Fraction $n/N+n$	Vapor Pressure Solution Calc.	Vapor Pressure Solution Obs.
Hexachlorethane	237	0.0793	332.2	332.3
Methyl salicylate	152	0.0920	327.5	329.7
Cyanic acid	43	0 0452	344.3	345.9
Trichloroacetic acid	163.5	0.1141	319.3	317.4
Aniline	93	0 0766	333.1	331.5

Raoult found that the average value of the relative lowering, $\frac{p_0 - p}{p_0}$, for fourteen different solutes was 0.0098 in 1 mol per cent solutions and this value is in good agreement with the calculated value

$$\frac{p_0 - p}{p_0} = \frac{n}{N + n} = \frac{1}{99 + 1} = 0.01.$$

* Raoult, Z. physik. Chem., **2**, 371 (1888).

When the solution is very dilute, the number of mols of solute is negligible in comparison with the number of mols of solvent, and the equation of Raoult may be written in the form,

$$\frac{p_0 - p}{p_0} = \frac{n}{N}. \tag{4}$$

Since $n = g/m$, and $N = W/M$, where g and W are the weights of solute and solvent, respectively, and m and M are the corresponding molecular weights, the above equation becomes

$$\frac{p_0 - p}{p_0} = \frac{gM}{Wm}. \tag{5}$$

This equation enables us to calculate the molecular weight of a dissolved substance from the relative lowering of the vapor pressure produced by the solution of a known weight of solute in a known weight of solvent. Solving the equation for m, we have

$$m = \frac{gM}{W} \cdot \frac{p_0}{p_0 - p}. \tag{6}$$

As an illustration of the application of this equation, we may take the determination of the molecular weight of ethyl benzoate from the following experimental data: — The vapor pressure at 80° C. of a solution of 2.47 grams of ethyl benzoate in 100 grams of benzene is 742.6 mm.: the vapor pressure of pure benzene at 80° C. is 751.86 mm. Substituting in the equation, we have

$$m = \frac{2.47 \times 78}{100} \cdot \frac{751.86}{751.86 - 742.6} = 156.$$

The molecular weight calculated from the formula, $C_6H_5COO \cdot C_2H_5$, is 150.

The Measurement of Vapor Pressure. The difficulties which attend the accurate measurement of the vapor pressure of a solution by the static method have already been mentioned. Although there are other methods which are preferable for the determination of the molecular weight of dissolved substances, the vapor-pressure method has one marked advantage — it can be used for the same solution at widely divergent temperatures. The method devised by Walker, and already described in connection with the determination of the vapor pressure of pure liquids (p. 48), is well adapted to the measurement of the vapor pressure of solutions.

The fundamental importance of accurate determinations of the lowering of the vapor pressure of various solvents by dissolved substances

has long been recognized. With this end in view, the inherent defects in both the static and dynamic methods have been made the subject of numerous investigations, and during recent years improved forms of apparatus have been developed which have raised these methods to the rank of methods of precision.

The outstanding difficulties in all static methods are: (1) the complete removal, from the solution, of dissolved gases and other constituents more volatile than the solvent; and (2) the prevention of inequalities in concentration throughout the solution. These difficulties have been almost completely overcome by Frazer and Lovelace,* who

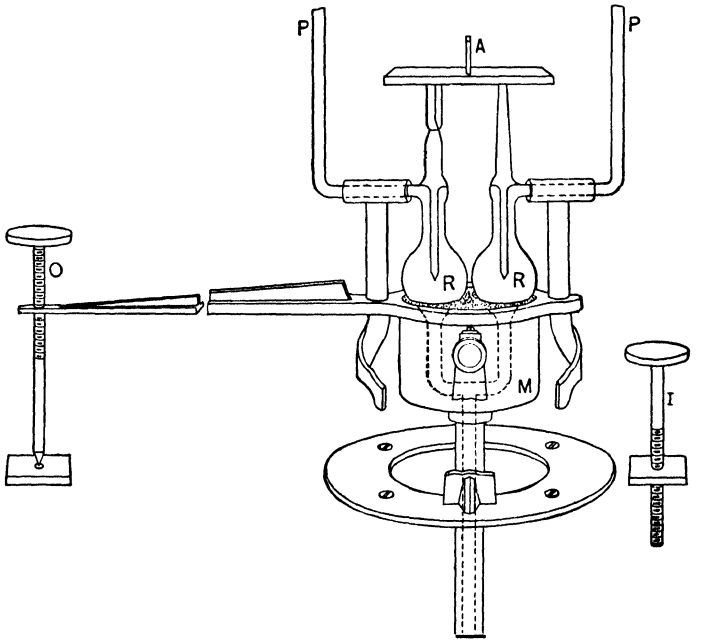


FIG. 64

have devised a form of apparatus in which provision is made for the removal of dissolved air, and for complete renewal of the entire surface of the solution by vigorous stirring. In this apparatus, use is made of the principle of the Rayleigh manometer† to measure the difference between the vapor pressure of the solution and that of the pure solvent. The essential features of this extremely sensitive pressure gauge are shown in Fig. 64.

* J. Am. Chem. Soc., **36**, 2439 (1914).

† Trans. Roy. Soc., **196**, 205 (1901).

The tubes P and P connect the two systems, solvent and solution, with the differential mercury manometer. This manometer consists of the U-tube M, which ends in the two bulbs R and R, which are about 4 cm. in diameter. It is connected through a rubber tube with a mercury reservoir which may be adjusted very accurately to any desired height by means of the screw I. The leveling screw O is arranged to tilt the manometer very slightly, and the extent to which it is tilted may be determined accurately by reflecting a beam of light from the vertical mirror A onto a vertical scale. The zero position on the scale is determined while both tubes are connected to the solvent by adjusting the level of the mercury and tilting the manometer until the two pointers just touch the surface of the mercury as determined with a microscope.

One side of the manometer is then connected with the solution which has a lower pressure. The two screws I and O are again turned until the pointers just touch the surface of the mercury, and the difference in levels of the mercury in the manometer is determined from the scale with the help of trigonometrical relations.

If d represents the distance between the points, D the distance from mirror to scale, θ the angle of tilting from the zero position, h the difference in pressure in the two limbs of the manometer corresponding to this angle of tilting, and S the scale deflection, then the following equations are obtained:

$$h = d \sin \theta \quad \text{and} \quad S = D \tan 2\theta;$$

and

$$h = \frac{d\,S}{2\,D} \frac{\sin \theta}{\frac{1}{2} \tan 2\theta}. \tag{7}$$

Now for all values of θ up to 1°, $\frac{\sin \theta}{\frac{1}{2} \tan 2\theta}$ may be regarded as unity and our formula becomes, $h = d\,S/2\,D$. For the particular instrument described here an angle of 1° in θ corresponds approximately to the depression of a 3-molar solution of a non-electrolyte. $d = 38.88$ mm. and $D = 3350.6$ mm. Substituting these values and making $S = 1$ we get $h = \frac{38.88 \times 1}{2 \times 3350.6} = 0.00580$. This means that 1 mm. scale deflection from zero position corresponds to a difference in pressure in the two bulbs of 0.00580 mm.

In using an instrument of such precision the authors are subjecting the static method of measuring vapor pressures to the severest test that could be applied. The results, however, have fully justified its use.

In the following table are given the results of a series of measure-

ments of the lowering of the vapor pressure of water produced by mannitol.

VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF MANNITOL*
(Temperature 20°)

Molal Conc.	Vapor Pressure Lowering in mm.		Lowering per Mol Solute (Obs.)
	(Obs.)	(Calc.)	
0.0984	0.0307	0.0311	0.3113
0.1977	0.0614	0.0622	0.3108
0.2962	0.0922	0.0931	0.3133
0.3945	0.1227	0.1239	0.3107
0.4938	0.1536	0.1547	0.3111
0.5944	0.1860	x	0.3129
0.6934	0.2162	0.2164	0.3118
0.7927	0.2478	0.2469	0.3126
0.8922	0 2792	0 2775	0.3129
0.9908	0 3096	0 3076	0.3124

* Frazer, Lovelace and Rogers, J. Am. Chem. Soc., **42**, 1793 (1920).

In the dynamic, or air-saturation, method of determining vapor pressures, the chief sources of error are: (1) in the measurement of the volume of aspirated air, and (2) in maintaining a constant temperature during the successive determinations of the vapor pressures of the solvent and the solution. These difficulties may be overcome by so arranging the apparatus that the same quantity of air is passed over the solution and solvent in succession, both liquids being contained in similar "saturators" which are immersed in a thermostat. The losses in weight of solution and solvent, due to the removal of the vapor of the latter, may be determined either by weighing the saturators before and after an experiment, or by absorbing the moisture, which is present in the saturated air, in suitable weighed absorption apparatus. The former method has been followed by Berkeley, Hartley, and Burton†; Washburn and Heuse‡ have adopted the latter. Both methods give excellent results.

Elevation of the Boiling-Point. Since the vapor pressure of a solvent is lowered by the addition of a non-volatile solute, it is obvious that the solution must be heated to a higher temperature than the

† Trans. Roy. Soc., **A 209**, 177 (1909); **A 218**, 295 (1919).

‡ J. Am. Chem. Soc., **37**, 309 (1915).

solvent in order that both may have the same vapor pressure. This fact is shown in Fig. 65, where the curve for the vapor pressure of the solution is seen to cut the line of barometric pressure at a higher temperature than does the curve representing the vapor pressure of the solvent. p_1 is the pressure (760 mm.) at which both the solvent and the solution boil, T_1 is the boiling temperature of the solvent at this pressure, and T_2 the boiling-point of the solution. p_2 is the vapor pressure of the pure solvent at T_2, the temperature at which the solution boils.

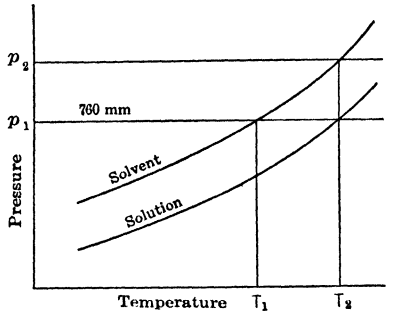


FIG. 65

According to Raoult's law, the vapor pressure of the solvent in the solution is equal to the mol fraction of the solvent, y, multiplied by the vapor pressure of the pure solvent, and therefore at temperature T_2

$$p_1 = yp_2. \tag{8}$$

Taking logarithms of this equation,

$$\ln p_1 = \ln y + \ln p_2 \quad \text{or} \quad -\ln y = \ln p_2 - \ln p_1. \tag{9}$$

But according to the Clausius-Clapeyron equation,

$$\ln p_2 - \ln p_1 = \frac{L\,(T_2 - T_1)}{RT_2T_1} \tag{10}$$

where L is the molar heat of vaporization and R is the molar gas constant. Substituting

$$-\ln y = \frac{L\,(T_2 - T_1)}{RT_2T_1}. \tag{11}$$

Substituting the mol fraction of the solute x for the mol fraction of the solvent

$$y = 1 - x \tag{12}$$

$$-\ln y = -\ln (1 - x). \tag{13}$$

Designating the boiling-point elevation $T_2 - T_1$ by ΔT_b, and combining

$$-\ln (1 - x) = \frac{L\,\Delta T_b}{RT_2T_1}. \tag{14}$$

Now in *dilute* solutions three simplifications may be made as follows:

Expanding by MacLaurin's theorem,

$$-\ln (1 - x) = x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 + \ldots \tag{15}$$

and remembering that for small values of x the higher powers may be neglected in comparison with the first power,* we have

$$x = \frac{L\,\Delta T_b}{RT_2T_1}. \tag{16}$$

Furthermore, the number of mols of solute, n, is negligible in comparison with the number of mols of solvent, N, and

$$x = \frac{n}{N+n} = \frac{n}{N}. \tag{17}$$

Finally, the two temperatures being nearly the same we may write

$$T_2T_1 = T_1^2. \tag{18}$$

Making these changes

$$\Delta T_b = x\,\frac{RT_1^2}{L} = \frac{RT_1^2}{LN}\,n. \tag{19}$$

When the number of mols of solvent, N, is constant, RT_1^2/LN may be written as a constant, K, and

$$\Delta T_b = Kn. \tag{20}$$

In other words it has been proved that in dilute solutions the elevation of the boiling-point is proportional to the concentration of the solute.

Concentrations are usually expressed in terms of mols per 1000 grams of solvent, and K_b is designated as the molal elevation of the boiling-point — i.e., the value of ΔT_b when $n = 1$, and 1000 grams of solvent is used. It may be evaluated by substituting numerical values in equation (19). For water which boils at 100° C. with the absorption of 539 calories per gram,

$$K_b = \frac{RT_1^2}{LN} = \frac{1.99 \times 373^2}{(539 \times 18) \times \frac{1000}{18}} = 0.514. \tag{21}$$

The direct proportionality between the elevation of the boiling-point and the concentration of solute in dilute solutions has been abundantly verified by many experiments. In fact, the experimentally obtained value of the molal elevation K_b is used in preference to the thermodynamically determined value, but the two agree very closely. The accompanying table gives the molal boiling-point constants for some of the more common solvents, in very dilute solutions.

* For example, if $x = 0.01$, the expression becomes $0.01 + \frac{1}{2}\,0.0001 + \frac{1}{3}\,0.000001$, which is equal to 0.01 within one-half of one per cent.

MOLAL BOILING-POINT CONSTANTS

Solvent	Boiling-Point at 760 mm.	K_b	Correction per 10 cm.
Acetic acid	118 1	2.93	0.08
Benzene	80.3	2.43	0.24
Carbon disulphide	46.3	2.24	0.20
Chloroform	61.2	3.41	0.10
Ethyl alcohol	78.5	1.14	0.10
Ethyl ether	34.5	2.01	0 07
Ethyl acetate	77.1	2.52	0.12
Methyl alcohol	64.5	0 83	0 09
Methyl formate	31.8	1.42	0.10
Methyl acetate	57.1	1.92	0.09
Propyl alcohol	97.8	1.53	0.12
Water	100 00	0.512	0 07

The figures given in the last column are to be used in correcting the molal boiling-point constant for changes in barometric pressure; the corrections are to be added to K_b for every 10-mm. increase in pressure over 760 mm., and subtracted for every 10-mm. decrease below 760 mm.

In determining the molal elevation or the boiling-point constant, a small weight, g grams, of a solute of known molecular weight, m, is dissolved in G grams of solvent, and the elevation of the boiling-point, ΔT_b, is measured. The molal elevation, K_b, is then calculated as follows, on the assumption that the boiling-point elevation is proportional to the concentration.

$$\frac{g}{G} : \Delta T_b = \frac{m}{1000} : K_b, \tag{22}$$

therefore,

$$K_b = \frac{m\,\Delta T_b G}{1000\,g}. \tag{23}$$

It must be emphasized that the molal boiling-point constant is not the actual elevation of a 1-molal solution, but it is calculated for a 1-molal solution from data on dilute solutions.

Experimental Determination of Boiling-Points. The importance of molecular weights in establishing the formulas of new compounds has been discussed in an earlier chapter. Frequently it is impossible to vaporize the material for a vapor-density measurement on account of thermal decomposition, and the molecular weight m may then be determined from the elevation of the boiling-point which is produced

by dissolving the material in a suitable solvent. The calculation may be made with the help of the last formula and the known values of the molal elevations, that is,

$$m = 1000\, K_b \frac{g}{G\,\Delta T_b}. \tag{24}$$

In measuring the boiling-point of a solution, it is not possible to place the thermometer in the vapor, as in the case of a pure solvent, and it is particularly necessary to prevent superheating. One of the simplest and most convenient of the various forms of apparatus which have been devised for the determination of the boiling-points of solutions, is that developed by Mathews* from an earlier form of apparatus, described by Bigelow.† In this apparatus, the heat is supplied by an electric heating coil immersed in the solution. In this way superheating is eliminated and the measurements are easily made. A diagram of the apparatus is shown in Fig. 66. It consists of a boiling vessel, closed by a cork stopper, through which pass a Beckmann thermometer, the return tube from the condenser and the two small glass tubes containing the wires through which the current is led to the platinum heating coil. The boiling vessel is entirely enveloped within an un-silvered Dewar cylinder. Circulation of air between the boiling vessel and the vacuum jacket is prevented by means of a rubber gasket, or by cotton packing. The bulb of the thermometer is placed in the center of the large vertical coil, as shown in the diagram. Bubbles of vapor in rising do not touch the bulb of the thermometer, but rise directly to the surface of the liquid. The vortex motion produced by the ascending stream of bubbles serves to stir the liquid very effectively. The flattened bottom of the boiling vessel makes it possible to bring the heating coil so close to the lower end of the vessel that inequality of temperature, due to a more or less stagnant layer of liquid, is avoided. The heating elements consist of two strands of platinum wire 0.38 mm. in diameter and about 20 cm. in length. These are twisted together and a current of from 10 to 14 amperes is used. With a current of this strength there is far less superheating than when a coil of finer wire and greater length is used with a current of lower amperage. The constancy of the current is controlled by means of a suitable rheostat with a sliding contact. Inasmuch as constancy of boiling-point is largely dependent upon the constancy of the rate at which the condensed and cooled liquid returns from the condenser, it is very necessary that heat be supplied at a perfectly constant rate. The condensed liquid drops

* Trans. Am. Electrochem. Soc., **19**, 81 (1911).

† Am. Chem. J., **22**, 280 (1899).

freely from the condenser to the violently agitated boiling liquid below. Fluctuations in temperature always result if the liquid runs down the thermometer, the outside walls or the glass tubes, these fluctuations being due to imperfect mixing. A suitable weight of liquid is

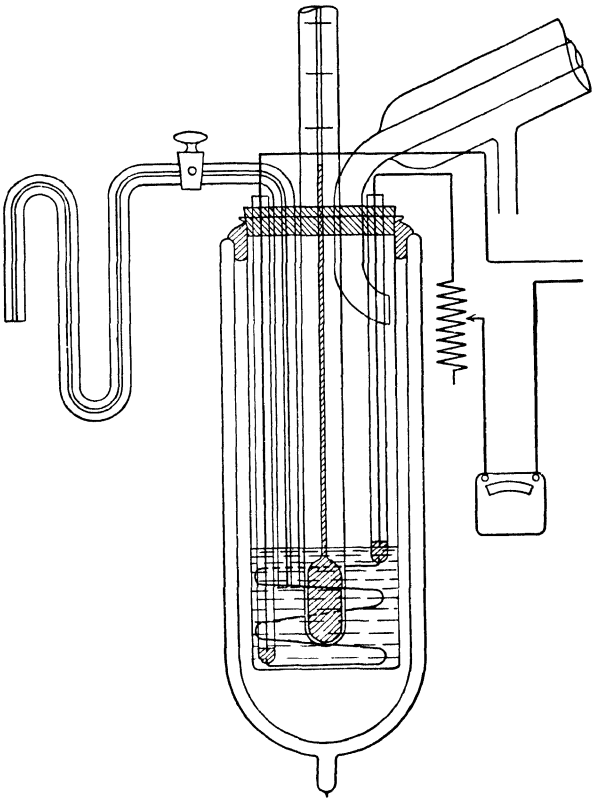


FIG. 66

boiled until the thermometer remains constant; this temperature is taken as the boiling-point of the liquid. A suitable amount of solute is added and the boiling-point of the solution is determined. By means of a capillary siphon a sample of the solution is removed for analysis. The difference between the readings of the thermometer when immersed in the solution, and in the solvent alone, gives the boiling-point elevation.

The accuracy of the results obtainable with the foregoing apparatus may be greatly enhanced by connecting it with a large reservoir and

manostat, in order that constant pressure may be maintained within the boiling vessel throughout an experiment.

The need of such pressure control is evident when one considers that the boiling-point of most solvents is changed 0.001° by a change in pressure of 0.03 to 0.04 mm. The pressure may be controlled to 0.02 mm. by a manometer which operates a relay through an electrical contact whenever the pressure falls below a specified value. The relay in turn opens a loosely operating stop-cock which allows compressed air to flow in until the pressure is reached. With this manostat and electric heating coil it is possible to keep the liquid boiling within 0.001° for over an hour at a time.*

Another form of boiling-point apparatus has been devised by Cottrell† by means of which it is possible to secure a perfect equilibrium between the liquid and vapor phases of a solution, and to determine with a high degree of accuracy the temperature of this equilibrium. The novel feature of this form of boiling-point apparatus consists in placing the thermometer bulb in the vapor phase, as in the case of a pure liquid, and causing the boiling liquid to pump some of itself over the thermometer bulb in a thin film without superheating.

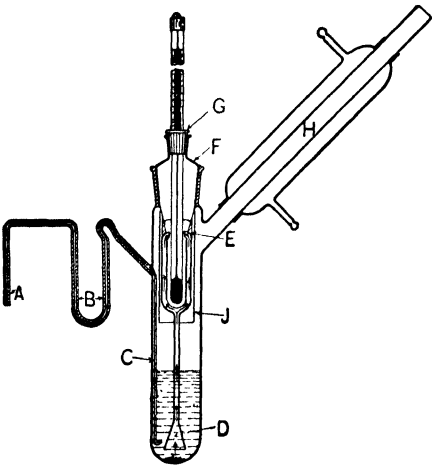


FIG. 67

The apparatus is shown diagrammatically in Fig. 67. The tube *D* functions as a pump, and insures the passage of an intimate mixture of solution and vapor over the thermometer bulb. A glass sheath *J* is attached to the ground-glass stopper and serves to protect the thermometer bulb from the cooling influence of the condensed solvent as it flows back into the boiling vessel. The solute is introduced through the condenser tube *H*. When the boiling-point of a solution becomes constant to within 0.001°, the source of heat is momentarily removed and the capillary U-tube, *B*, is surrounded by a bath of ice water. By applying air pressure at the open end of the condenser tube, *H*, a sample of the solution can be

* Carroll, Rollefson and Mathews, J. Am. Chem. Soc., **47**, 1791 (1925).

† J. Am. Chem. Soc., **41**, 721–732 (1919).

removed for analysis. In this way the exact concentration of the liquid phase can be obtained.

The following table contains the results of an investigation on the boiling-points of solutions of naphthalene in benzene carried out with the Cottrell apparatus by Washburn and Read.*

The figures in the first column give the values of the measured elevations of the boiling-point, while those of the second column give the corresponding concentrations expressed as mol fractions of solute. The values of the concentrations, calculated on the assumption that the solutions obey Raoult's law, are given in the last column.

BOILING-POINTS OF SOLUTIONS OF NAPHTHALENE IN BENZENE

ΔT_b(obs.)	x_1 (obs.)	x_1 (calc.)
1.478	0.04169	0.04293
2.430	0 07012	0.06938
3 890	0 10779	0.10820
4.967	0.13529	0.13553
5.238	0.14220	0.14236
6 368	0.17204	0.16947

Lowering of the Freezing-Point. It has long been known that the freezing-point of water, or other liquid, is lowered by the addition of a solute, and it was pointed out by Blagden† over a century ago that the depression of the freezing-point is directly proportional to the concentration of the solution. The reason for the lowering will be understood with the help of Fig. 68. At the freezing-point the solid and the liquid are in equilibrium and both must have the same vapor pressure. If the solid has a greater pressure than the liquid, it will distil over into the liquid phase; if the liquid has the greater pressure, it will change into the solid. When the vapor pressure of a solvent is lowered by the addition of a solute, the solid will disappear if the temperature is maintained constant, but a state of

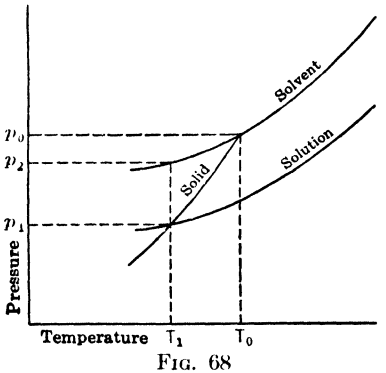


FIG. 68

† Phil. Trans., **78**, 277 (1788).

* J. Am. Chem. Soc., **41**, 729 (1919).

equilibrium may be effected by lowering the temperature. It will be remembered that the vapor pressure-temperature curve of a solid is steeper than that of the corresponding liquid because the heat of sublimation is greater. At the intersection of the two curves, solid and liquid are in equilibrium, and the corresponding temperature is the freezing-point. The greater the concentration of the solution, the lower is the vapor-pressure and the lower is the freezing-point. The quantitative relation between the concentration of the solution and the freezing-point depression can be derived from the Clausius-Clapeyron equation as shown below.

The freezing-point of the pure solvent is given in Fig. 68 by T_0 and that of the solution by T_1. The corresponding pressures are p_0 and p_1, and p_2 is the vapor pressure of the pure solvent supercooled to the freezing-point of the solution.

The sublimation curve of the solid is connected with the molar heat of sublimation, L_s, as follows:

$$\ln p_0 - \ln p_1 = \frac{L_s(T_0 - T_1)}{RT_0T_1}, \tag{25}$$

and in the same way the vapor-pressure curve of the liquid is connected with the molar heat of vaporization L_v as follows:

$$\ln p_0 - \ln p_2 = \frac{L_v(T_0 - T_1)}{RT_0T_1}. \tag{26}$$

Subtracting

$$(\ln p_0 - \ln p_1) - (\ln p_0 - \ln p_2) = \frac{(L_s - L_v)(T_0 - T_1)}{RT_0T_1}. \tag{27}$$

Combining, and remembering that the difference between the heat of sublimation and the heat of vaporization is equal to the molar heat of fusion, L_f,

$$\ln p_2 - \ln p_1 = \frac{L_f(T_0 - T_1)}{RT_0T_1}. \tag{28}$$

A substitution may be made on the basis of Raoult's law by setting y equal to the mol fraction of solvent as follows:

$$p_1 = yp_2, \tag{29}$$

or, taking logarithms,

$$-\ln y = \ln p_2 - \ln p_1. \tag{30}$$

Since the mol fraction of the solvent, y, is equal to $1 - x$ where x is the mol fraction of the solute

$$-\ln y = -\ln (1 - x). \tag{31}$$

Then, substituting

$$-\ln (1 - x) = \frac{L_f(T_0 - T_1)}{RT_0T_1}. \tag{32}$$

This is an exact equation for solutions which obey Raoult's law, provided the heat of fusion, L_f, is constant between T_0 and T_1, and provided the vapor obeys the simple gas law. In dilute solutions x is small and three simplifying approximations may be made as explained before (p. 168).

$$(a)\ -\ln (1 - x) = x. \qquad (b)\ x = \frac{n}{N} \qquad (c)\ T_0T_1 = T_0^2.$$

Then

$$\frac{n}{N} = \frac{L_f \Delta T_f}{RT_0^2}. \tag{33}$$

Or

$$\Delta T_f = \frac{RT_0^2}{L_f N} n = Kn. \tag{34}$$

The observed freezing-point depression $(T_0 - T_1)$ is ΔT_f.

MOLAL FREEZING-POINT CONSTANTS

Solvent	Freezing-Point	Molal Depression, K_f
Acetic acid	17	3 9
Benzene	5.4	5.12
Benzil	94	10 5
Bromine	−7.3	9.7
Ethylene bromide	10	12.5
Formic acid	8	2.8
Naphthalene	80	6.8
Nitrobenzene	5.7	7.0
Phenol	38.5	7.4
Tribromphenol	95	20.4
Urethane	49	5.14
Water	0	1.855
p-Xylol	16	4.3

The quantity K_f is defined as the freezing-point constant or molal depression. For water it has the value 1.86°, calculated as follows:

$$K_f = \frac{RT_0^2}{L_f N} = \frac{1.99 \times 273^2}{(18 \times 79.7) \times (\frac{1000}{18})} = 1.86. \tag{35}$$

In dilute aqueous solutions the freezing-point of water is lowered at the rate of 1.86° per mol of solute added to 1000 grams of water — i.e., $\Delta T_f = 1.86\ m$, where m is the molality of the solution.

The freezing-point constant may be evaluated also by direct experiment using a solute of known molecular weight, as in the case of the

boiling-point constant. The molecular weight, m, of solute may be calculated from the formula

$$m = 1000\, K_f \frac{g}{G\, \Delta T_f} \tag{36}$$

when g grams of solute is dissolved in G grams of solvent.

The freezing-point constants for a number of different solvents are given in the table opposite.

Experimental Determination of Freezing-Points. The most commonly used apparatus for determining freezing-points is that devised by Beckmann* and shown in Fig. 69. It consists of a thick-walled test tube, A, provided with a side tube and fitted into a wider tube, A_1. The whole is fitted into the cover of a large jar, which is filled with a freezing mixture whose temperature is several degrees below the freezing-point of the solvent. The tube A is closed by a cork stopper, through which pass the thermometer and stirrer. The thermometer is generally of the Beckmann differential type.

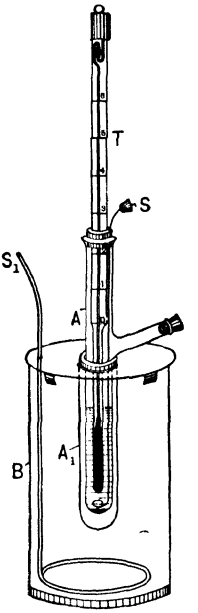


FIG. 69

In carrying out a determination with the Beckmann apparatus, a weighed quantity of solvent is placed in A, and the temperature of the refrigerating mixture is regulated so as to be not more than 5° below the freezing-point of the solvent. The tube A is removed from its jacket, and is immersed in the freezing mixture until the solvent begins to freeze. It is then replaced in the jacket A_1, and the solvent is vigorously stirred. The temperature rises as the liquid solidifies until the true freezing-point is reached, after which it remains constant. This temperature is taken as the freezing-point of the solvent. The tube A is now removed from the freezing mixture, and a weighed amount of the substance whose molecular weight is to be determined is introduced. When the substance has dissolved, the tube is replaced in A_1 and the solution cooled not more than a degree below its freezing-point. A small fragment of the solid solvent is dropped into the solution to relieve supersaturation, and the solution is stirred until the temperature is constant. The maximum temperature is taken as the freezing-point of the solution. The difference between the freezing-points of solution and solvent is the depression sought.

* Z. physik. Chem., **2**, 683 (1888).

In order to obtain trustworthy results with the freezing-point method, it is necessary that only the pure solvent separate out when the solution freezes and that excessive overcooling be avoided. When too great overcooling occurs, the subsequent freezing of the solution results in the separation of so large an amount of solvent in the solid state that the observed freezing-point corresponds to the equilibrium temperature of a more concentrated solution than that originally prepared.

If the overcooling of the solution in degrees is represented by u, the heat of fusion of 1 gram of solvent at the freezing-point by l_f, and the specific heat of the solvent by c, then the fraction, f, of the solvent which will solidify may be calculated by the formula,

$$f = \frac{cu}{l_f}. \tag{37}$$

When water is used as the solvent, $c = 1$ and $l_f = 80$. Therefore, for every degree of overcooling, the fraction of the solvent separating as ice will be 1/80, and the concentration of the original solution will be increased by just so much.

The foregoing method for the measurement of freezing-points is sufficiently accurate for ordinary laboratory requirements. For precise measurements, however, the following conditions are essential: — (1) rapid and certain attainment of the equilibrium temperature; (2) accurate measurement of the equilibrium temperature, preferably by means of a differential method in which the freezing-point depression is measured directly; and (3) exact determination of the concentration of the solution when equilibrium is attained. Numerous forms of apparatus have been designed with a view to meeting these conditions; one of the best is that devised by Adams.* In this form of apparatus the above requirements were satisfied as follows: — (1) by thoroughly mixing the solution with a large amount of finely crushed ice by means of an efficient stirrer; (2) by measuring directly the freezing-point depression by means of a multiple-junction thermoelement and sensitive potentiometer; and (3) by analyzing the equilibrium solution by means of special optical apparatus with which the concentration could be determined with an accuracy of two parts of solute in a million of solvent.

A diagram of the apparatus is shown in Fig. 70. Two similar vacuum-jacketed cylinders, A and B, are completely surrounded with crushed ice contained in a large felt-covered tank. The cylinder A contains about 400 grams of ice and 600 grams of water; the cylinder

* J. Am. Chem. Soc., **37**, 481 (1915).

B contains the same respective amounts of ice and solution. The liquid in each cylinder is thoroughly mixed by means of the valve-type stirrers *S,S*, which, when moved by the glass rods *R,R*, pump liquid from the bottom of each jar and discharge it over the ice. The difference in temperature between the contents of *A* and *B* is measured di-

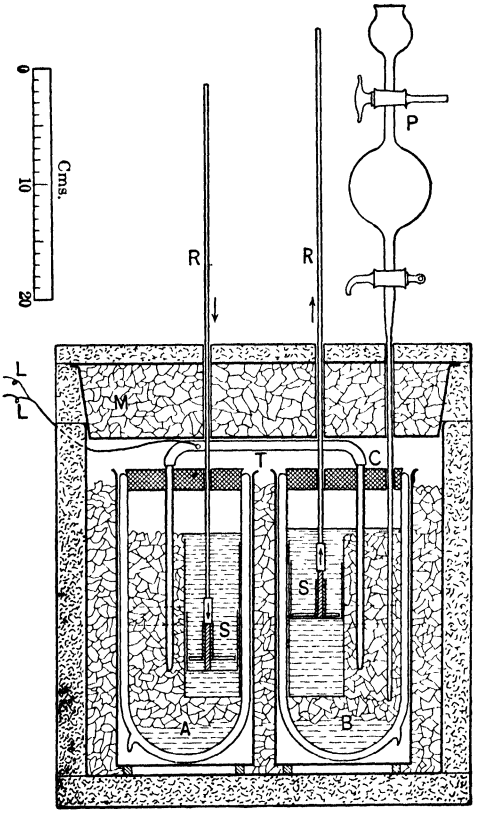


FIG. 70

rectly by means of the thermoelement *T*. When equilibrium is attained, a sample for analysis is withdrawn by means of *P*, which also serves to introduce both water and solution into *B*.

The following table gives the results of a series of determinations of the freezing-points of solutions of mannitol made with the Adams apparatus.

The third column contains the calculated values of the freezing-point depression. It will be seen that the solution follows the freezing-point

law very closely, i.e., the depression of the freezing-point is directly proportional to the concentration.

FREEZING-POINTS OF AQUEOUS SOLUTIONS OF MANNITOL*

Concentration in millimols per 1000 gm. H_2O. $n \times 10^3$	Freezing-Point Depression	
	ΔT_f (obs.)	ΔT_f (calc.)
4 02	0 0075	0.0075
8.42	0 0157	0.0156
14.04	0 0260	0.0261
28 29	0 0525	0 0525
62.59	0.1162	0.1162

* Adams, loc. cit.

Osmosis. Closely related to the lowering of the freezing-point and the lowering of the vapor pressure is the phenomenon of osmosis, i.e., the passage of a solvent through a membrane from a dilute solution into a more concentrated one. This phenomenon was first observed in 1748 by Abbé Nollet but it was not until the middle of the following century that further investigations were carried out by Dutrochet and Vierordt. As a result of their studies it was found that, when a salt solution is separated from water by a suitable animal membrane, the water diffused through the membrane more rapidly than did the salt. The level of the solution rose, causing an appreciable hydrostatic pressure to develop. Since this pressure was caused by the process of osmosis, it was called osmotic pressure.

Traube in 1867 substituted artificial membranes for the animal membranes which had been used in the earlier investigations of osmosis. He showed that a gelatinous precipitate of copper ferrocyanide is particularly effective as a *semi-permeable membrane* permitting the free passage of water but preventing the passage of dissolved material. If a glass tube provided with a rubber tube and pinch-cock is partially filled by suction with a solution of copper sulphate and then immersed in a dilute solution of ferrocyanide, a thin film of copper ferrocyanide will be formed at the junction of the two solutions. When the film has once been formed, further precipitation of copper ferrocyanide ceases but water passes through toward the region of higher concentration of dissolved material and ruptures the membrane. For quantitative measurements of osmotic pressure the precipitate of copper

ferrocyanide is formed by the method of Morse* in the pores of a porous clay cup. The cup is filled with potassium ferrocyanide and set into a solution of copper sulphate; a current of electricity is then passed through so that copper and ferrocyanide ions migrate toward each other and precipitate within the walls of the cup.

Mechanism of Osmosis. Many theories have been proposed to explain the passage of solvent through a semi-permeable membrane from a dilute solution to a more concentrated one. According to the simplest of these the solvent merely moves from a region where its escaping tendency is large (its vapor pressure is high) to a region where its escaping tendency is small. The membrane is so constituted that the dissolved material cannot pass. The presence of the dissolved material lowers the escaping tendency of the solvent, and the greater the concentration, the greater is the lowering.

The simplest illustration is offered by setting a dish containing pure water and a dish containing a solution of sugar or other material into an enclosed vessel, such as an empty desiccator, and immersing it in a thermostat. After standing, the level of the solution will rise and the level of the pure water will fall due to the diffusion of the water from the pure solvent, where the vapor pressure is high, to the solution, where the vapor pressure is relatively low.

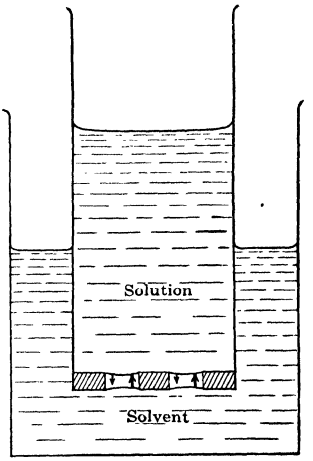


FIG. 71

One of the ways in which a semi-permeable membrane may function is shown schematically in Fig. 71. Very small passages exist in the semi-permeable membrane, so small that the liquids are kept from flowing through by surface tension even if a large hydrostatic pressure is applied. But the solvent molecules can still pass through in the vapor phase as individual molecules, and there will be a steady migration from the solvent to the solution as indicated by the arrows representing vapor pressures — the heavier arrow indicating the higher vapor pressure of the solvent. As in the case of the separate vessels described in the preceding paragraph the solvent molecules are free to migrate but the solute molecules cannot bridge the gap. That this mechanism is possible has been proved by the osmosis which occurs when a solution is separated from a solvent by a glass tube containing many infinitesimal cracks.

* Carnegie Inst. Publ., 198 (1914).

In many cases the semi-permeable membrane is more than a system of minute passages, available for gas diffusion but not for liquid diffusion. Animal membranes and certain gels offer a medium for the diffusion of water but not for the diffusion of the solute. Solubility of the solvent in the membrane is another way in which a semi-permeable membrane may be produced. For example, if a rubber membrane separates a solution of sugar in pyridine from pure pyridine, the pyridine dissolves in the rubber and passes through from the solvent into the solution.

Nature of the Membrane. Ostwald demonstrated theoretically that the pressure due to osmosis must be independent of the nature of the membrane employed in measuring it. Thus, in Fig. 72, A and B represent two different semi-permeable membranes in an imaginary apparatus. The space between is filled with solution and the end spaces are filled with pure solvent. If the nature of the membrane has any influence on the osmotic pressure, the osmotic pressure P_B may be imagined greater than the osmotic pressure P_A and under this condition the solvent will be forced out toward the left. It may be collected at this higher pressure and returned to the right through a turbine which may be made to do mechanical work. After being returned to the compartment at the right it will flow into the solution and thence through the cycle repeatedly. But such an arrangement would be a means of producing energy at constant temperature in a cyclic process. Since such perpetual motion is impossible the premise of two different membranes must be wrong and all semi-permeable membranes must give the same osmotic pressure.

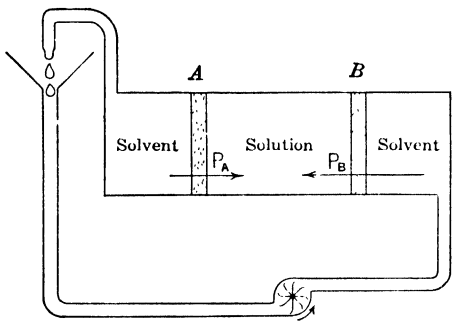


FIG. 72

In actual practice different membranes may appear to give different hydrostatic pressures, but if sufficient time is allowed for the attainment of equilibrium, and if the membrane does not leak, the pressures will ultimately be the same. The nature of the membrane and its area determine how *rapidly* osmosis occurs. If any solute diffuses into the solvent, the membrane is not truly semi-permeable.

Osmotic Pressure. The first direct measurements of osmotic pressure were made by the botanist, Pfeffer, in 1877. Using a closed-end mercury manometer he was able to measure the hydrostatic

pressure generated in a solution by the ingress of water through a semi-permeable membrane without serious dilution of the solution. Pfeffer's results are given in the following tables because they constituted the foundation of the development of the classical theory of solutions. The concentration of cane sugar in percentage is given under C, the osmotic pressure in atmospheres under P, and the absolute temperature under T.

RELATION OF OSMOTIC PRESSURE TO CONCENTRATION
TEMPERATURE, 286.5° to 287.7°

C	P	P/C
1	0.70	0.70
2	1.34	0.67
4	2.74	0 68
6	4 10	0 68

RELATION OF OSMOTIC PRESSURE TO TEMPERATURE
CONCENTRATION, 1 PER CENT

T	P	P/T
273 0	0.649	0 238
279.8	0.664	0 237
286.7	0.691	0 241
288.5	0.684	0 237
295	0.721	0 244
305	0.716	0 235
309	0 746	0 241

The significance of Pfeffer's measurements was first perceived by van't Hoff,* who pointed out the existence of a striking parallelism between the properties of gases and the osmotic properties of solutions. The ratio P/C is nearly constant for any one solute, and since the concentration varies inversely as the volume in which a definite amount of solute is dissolved, we find, on substituting $1/V$ for C, that PV = constant. This relation is the same as Boyle's law for gases. It is evident also that P/T is nearly a constant, i.e, that the osmotic pressure is directly proportional to the absolute temperature. Again this relation is identical with the familiar Gay-Lussac law for gases.

* Z. physik. Chem., **1**, 481 (1887).

Hence it is possible, as in the case of gases, to construct a general equation

$$PV = nR'T \tag{38}$$

where P is osmotic pressure and R' is a constant.

In a 1 per cent solution, 34.2 liters of solution are required to hold 1 mol of sugar. Combining this fact with Pfeffer's data at 0°, van't Hoff calculated the value of the constant R' as follows:

$$R' = \frac{PV}{T} = \frac{0.649 \times 34.2}{273} = 0.0813 \text{ liter-atmospheres.} \tag{39}$$

This constant R' obtained from osmotic data has practically the same value as the gas constant R, viz., 0.0821. It may be concluded then that in dilute solutions the gas laws may be applied to solutions, and molecular weights of dissolved substances may be calculated from osmotic pressures or osmotic pressures may be calculated from concentrations with the help of the familiar equation

$$PV = \frac{g}{M}RT. \tag{40}$$

For example, if 1.00 gram of sugar having a molecular weight of 342 is dissolved in 50 cc. of solution at 25° C. the osmotic pressure will be 1.43 atmospheres, for

$$P = \frac{g}{M}\frac{RT}{V} = \frac{1 \times 0.082 \times 298}{342 \times .050} = 1.43.$$

It must be emphasized that this formula holds only for dilute solutions where the volume of the solute is negligible in comparison with that occupied by the solvent.

Measurement of Osmotic Pressure. Accurate measurements of osmotic pressure have been made by Morse and his co-workers* and also by the Earl of Berkeley and Hartley.† Morse's apparatus was similar in principle to Pfeffer's, the solution being allowed to build up a measured hydrostatic pressure through a specially prepared porous cup containing precipitated copper ferrocyanide.

The following table, taken from the papers of Morse and his students, shows that, when concentrations are expressed on the molal basis, there is direct proportionality between osmotic pressure and concentration over a comparatively wide range of both concentration and temperature.

* Carnegie Inst. Publ., 198 (1914).

† Trans. Roy. Soc., **A 206**, 481 (1906).

OSMOTIC PRESSURES OF SUCROSE SOLUTIONS IN ATMOSPHERES

Conc. Mols per 1000 g. Solvent	0°		20°		40°		60°		Av. Ratio
	Press.	Ratio	Press.	Ratio	Press.	Ratio	Press.	Ratio	
0.1	2.462	1.106	2.590	1.130	2.560	0.998	2.717	1.000	1.06
0.2	4.723	1.065	5.064	1.060	5.163	1.012	5.438	1.001	1.03
0.4	9.443	1.060	10.137	1.060	10.599	1.037	10.866	1.000	1.04
0.6	14.381	1.077	15.388	1.071	16.146	1.053	16.535	1.015	1.05
0.8	19.476	1.091	20.905	1.093	21.806	1.068	22.327	1.025	1.07
1.0	24.826	1.130	26.638	1.130	27.701	1.085	28.367	1.045	1.10

In the columns headed "Ratio" are given the ratios of the measured values of osmotic pressure to the corresponding calculated values.

It may be concluded that the gas laws apply up to concentrations of 1 molal, if the concentrations are referred to mols per 1000 g. of solvent, whereas they do not hold satisfactorily when the concentration is referred to the volume of the solution. The correction for the volume of the solute molecules is similar to the correction applied in van der Waals' equation for the volume, b, of the gas molecules.

The apparatus of Berkeley and Hartley is shown diagrammatically in Fig. 73. A membrane of copper ferrocyanide is deposited electrolytically very near the outer surface of a tube of porous porcelain. This tube is placed co-axially within a large cylindrical vessel of gun metal, an absolutely tight joint between the two being secured by an ingenious system of rings and clamps. The open ends of the porcelain tube are closed by rubber stoppers fitted with capillary tubes bent at right angles, one of the latter being provided with a glass stopcock. When a determination of osmotic pressure is to be made, the apparatus is placed in a horizontal position and water is introduced into the porcelain tube, completely filling it and the connecting capillary tubes up to a certain level. The gun metal vessel is then filled with the solution, and connected with an auxiliary apparatus by means of which a gradually increasing hydrostatic pressure can be applied. If insufficient pressure is applied to the solution, water will pass through the

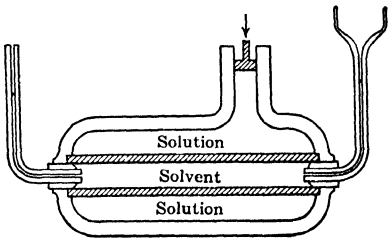


FIG. 73

semi-permeable membrane into the solution, and the level of the water in the capillary tubes will fall. If too much pressure is applied the level will rise. When the level of the water in the capillary tubes remains constant, the two pressures are in equilibrium and the hydrostatic pressure applied to the solution is equal to the osmotic pressure. After carrying out an experiment the water is tested for solute to make

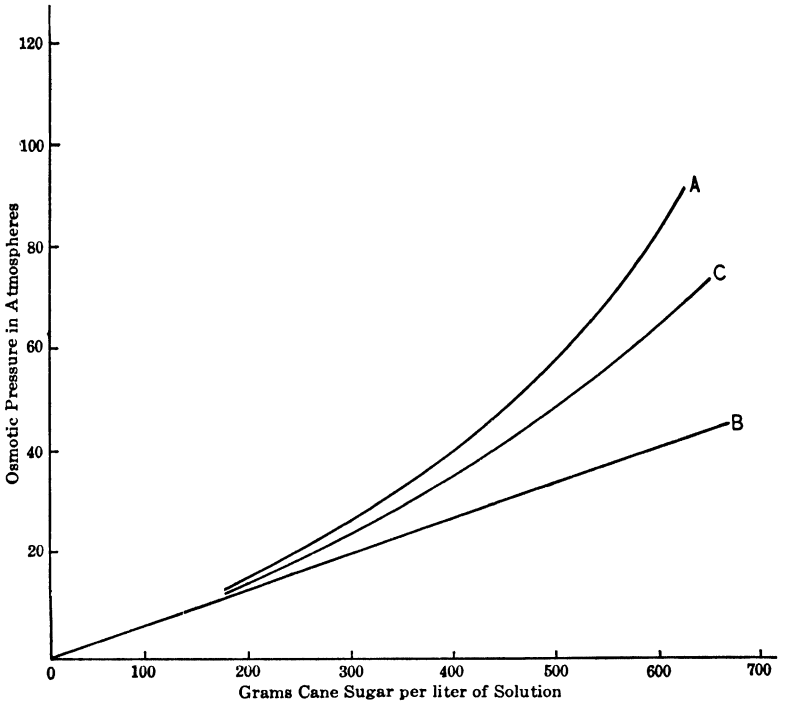


FIG. 74

certain that the semi-permeable membrane has not failed. The membranes were found to hold perfectly even when the pressure was over 100 atmospheres.

Typical results are shown in the following table where they are compared with the theoretical values taking the volume as the volume of the solution. The results are shown also in Fig. 74, where the osmotic pressures of solutions of cane sugar are plotted against concentrations. Curve A represents the actually observed osmotic pressures; curve C is traced on the assumption that osmotic pressure may be calculated from the equation, $PV = RT$, where V denotes the volume of solvent containing 1 mol of cane sugar; and curve B, a straight line, is drawn

on the assumption that osmotic pressure may be calculated from the equation, $PV = RT$, where V represents the volume of solution containing 1 mol.

OSMOTIC PRESSURE OF SUCROSE SOLUTIONS

(Temperature 0°)

Conc. g. per Liter	Press. (Obs.) Atmospheres	Press. (Calc.) Atmospheres
180.1	13.95	13.95
300.2	26.77	28.74
420.3	43.97	32.55
540 4	67.51	41.85
660 5	100.78	51.16
750.6	133.74	58.14

While the theoretical and observed values of the osmotic pressure are approximately equal in the more dilute solutions, it is obvious that the observed values of the osmotic pressure of the concentrated solutions are always greater than the calculated values, even when the calculation is made on the assumption that V in the equation $PV = RT$ is the volume of the solvent. This discrepancy between experiment and theory in concentrated solutions is not peculiar to osmotic pressure. Ideal solutions are very rare, and we have to accept the fact that the behavior of concentrated solutions is too complicated to be explained by the simple laws which we have thus far developed. Undoubtedly the nature of the solvent itself is affected by the presence of a high concentration of solute.

OSMOTIC PRESSURE OF SUCROSE SOLUTIONS

(Temperature 30°)

Conc. g. per 1000 g. H_2O	Press. (F. & M.) Atmospheres	Press. (B. & H.) Atmospheres
202	15.59	15.48
370	29.78	29.72
569	47 88	48.81
820	73.06	74.94
1133	109.10	111.87
1430	148 80	148.46

Frazer and Myrick* modified the original apparatus of Morse so as to make measurements up to 270 atmospheres under conditions requiring only a few hours for equilibrium. The solution is allowed to develop its own equilibrium and the pressure is determined with an electrical gauge, which utilizes the principle that the resistance of certain metallic conductors increases linearly with the pressure. In the preceding table their results are compared with those of Berkeley and Hartley, corrected to the same temperature.

Comparison of Experimental Methods. The four properties of solutions which have just been studied, vapor-pressure lowering, boiling-point elevation, freezing-point lowering and osmotic pressure, are sometimes called the colligative properties of solutions on account of their inter-relationship. Of these, the freezing-point lowering can be measured most accurately and most easily and the osmotic pressure can be measured least accurately and only with great difficulty. The freezing-point method is limited to low temperatures where the solubility is often small. The boiling-point readings may be seriously affected by fluctuations in the barometric pressure, and in the case of water, the molal elevation is only about one-third as great as the freezing-point depression. The temperature range is limited also in the case of the boiling-point method. The vapor-pressure lowering is adaptable to different temperatures and capable of high accuracy, but it requires more elaborate apparatus. Osmotic pressure was most used in the early development of the theory of solutions and it is the most important historically, but at present the concept of vapor-pressure lowering seems to be more useful in the theoretical treatment of solutions.

Thermodynamic Relations. It has been shown that the four colligative properties may be readily calculated in dilute solutions, but that the simple formulas fail when applied to concentrated solutions. It is a necessary consequence of thermodynamics, however, that at the same temperature the deviations from ideal solutions are the same in all the different properties. For example, if the vapor-pressure lowering is known, the osmotic pressure may be calculated with exactness, even in concentrated solutions where Raoult's law does not hold and where the osmotic pressure cannot be calculated from the gas laws. These relations follow from the fact that the free energy of dilution is the same no matter whether it is effected by evaporation, by freezing, or by application of pressure through a semi-permeable membrane.

Imagine a large reservoir of solution having a vapor pressure p, and near it a reservoir of pure solvent at the vapor pressure p_0. One mol

* J. Am. Chem. Soc., **38**, 1907 (1916).

of vapor is evaporated reversibly from the solution (by keeping the pressure infinitesimally less than p), and then it is compressed reversibly from pressure p and volume v to pressure p_0 and volume v_0. The quantity of solution is so great that the removal of 1 mol of the solvent does not appreciably increase the concentration of the solution. After compressing to p_0, the mol of vapor is condensed reversibly in the pure solvent by applying a pressure infinitesimally greater than p_0. The work involved in these steps is maximum work because the steps are all carried out under conditions approaching equilibrium. Assuming that the vapor behaves as an ideal gas, the work expended in this condensation and the work obtained in evaporation are both equal to RT and hence are equal to each other. All the steps are carried out isothermally, and the free energy increase is represented by the following equations.

Referring back to p. 132,

$$\Delta F = \Delta A + RT \ln \frac{v_0}{v} + RT \ln \frac{p_0}{p} \tag{41}$$

but

$$\Delta A = -w_{\max} = -RT \ln \frac{v_0}{v} \tag{42}$$

and

$$\Delta F = RT \ln \frac{p_0}{p}. \tag{43}$$

Now this transfer of 1 mol of solvent from the solution to the solvent can also be effected by osmosis. The solution is placed in a cylinder, provided with a movable semi-permeable membrane for a piston, and a pressure is applied infinitesimally greater than the osmotic pressure, P. The work done in removing 1 mol of solvent* is PV' where V' is the molar volume of the solvent. The work done is maximum work, and no work is done against the atmosphere because the volume of a mol of solvent is practically unchanged when added to the solution. Hence

$$PV' = \Delta F, \tag{44}$$

and combining with equation (43)

$$PV' = RT \ln \frac{p_0}{p}, \tag{45}$$

$$P = \frac{RT}{V'} \ln \frac{p_0}{p}. \tag{46}$$

With this formula it is possible to calculate the osmotic pressure of a solution from the vapor pressures of the solvent and the solution, and

* It is assumed here that the molecular weight is the same in the liquid and gaseous states. If it is not, sufficient liquid is removed to produce 1 mol of vapor.

the molar volume of the solvent. At high concentrations, where the osmotic pressures calculated by the simple gas laws (equation 40) are in error by over 30 per cent, the values calculated by equation (46) check with the observed values within less than 1 per cent.

For ideal solutions or dilute solutions, where Raoult's law holds,

$$p = p_0 y$$

where y is the mol fraction of the solvent, and

$$\ln \frac{p_0}{p} = -\ln y. \tag{47}$$

Since the mol fraction y of the solvent is equal to $1 - x$, where x is the mol fraction of the solute

$$\ln y = \ln (1 - x). \tag{48}$$

Then

$$P = \frac{RT}{V'} [-\ln (1 - x)]. \tag{49}$$

Expanding in a series

$$P = \frac{RT}{V'} (x + \tfrac{1}{2} x^2 + \tfrac{1}{3} x^3 + \cdots). \tag{50}$$

When x is small, higher powers may be neglected and

$$PV' = xRT. \tag{51}$$

But $x = n/(n + N)$ and in dilute solutions $x = n/N$, where n is the number of mols of solute and N the number of mols of solvent. When $n = 1$, N is the number of mols of solvent containing 1 mol of solute, and

$$PV'N = RT. \tag{52}$$

Setting V, the volume of the dilute solution containing 1 mol, equal to $V'N$,

$$PV = RT. \tag{53}$$

This is equivalent to (38), discovered experimentally, and it is evident from the approximations introduced why it cannot hold for concentrated solutions.

The free energy of transfer given by equation (43) may be applied to solutions of different concentrations as well as to a solution and the pure solvent. It finds important applications which will be studied in a later chapter. In dilute solutions it is permissible to write as approximate formulas,

$$\Delta F = RT \ln \frac{p_2}{p_1} = RT \ln \frac{y_2}{y_1} = RT \ln \frac{c_2}{c_1} \tag{54}$$

where y_1 represents the mol fraction and c_1 the concentration of the substance in a solution having a vapor pressure p_1 and y_2, c_2 and p_2 refer to the same properties in a solution of different concentration.

REFERENCES

Osmotic Pressure. Alexander Findlay.
Solubility. J. H. Hildebrand.
Osmotic Pressure. Symposium of the Faraday Society. (1917.)

PROBLEMS

1. The vapor pressure of ether at 20° C. is 442 mm. and that of a solution of 6.1 g. of benzoic acid in 50 g. of ether is 410 mm. at the same temperature. Calculate the molecular weight of benzoic acid in ether. *Ans.* 125.

2. The vapor pressure of a solution containing 11 g. of solute in 100 g. of H_2O at 25° is 23.110 mm. Calculate the molecular weight of the solute. The vapor pressure of water at this temperature is 23.756 mm.

3. The vapor pressure of ether at 20° is 442 mm. What is the vapor pressure of a solution containing 10 g. of benzaldehyde in 100 g. of ether? *Ans.* 411 mm.

4. Calculate the vapor pressure of a 20 per cent sugar solution at 25°. The vapor pressure of water at this temperature is 23.756 mm.

5. A solution containing 0.7269 g. of camphor (mol. wt. = 152) in 32.08 g. of acetone (boiling-point = 56.30° C.) boiled at 56.55° C. (*a*) What is the molar elevation of the boiling-point of acetone? (*b*) What is its heat of vaporization?
(*a*) 1.68°. (*b*) 128.6 cals. per gram.

6. The heat of vaporization of benzene is 394.8 joules/gram and its boiling-point 353.35° K. A solution containing 0.698 g. of substance in 63.88 g. benzene raised the boiling-point 0.145°. Calculate the molecular weight of the solute.

7. Calculate the heat of vaporization of ether from these data: The solution of 1.027 g. of naphthalene in 80.24 g. of ether raised the boiling-point 0.2148° above its normal boiling-point, 34.60°. The experimental value is 351 joules/gram.

8. The freezing-point of pure benzene is 5.440° and that of a solution containing 2.093 g. of benzaldehyde in 100 g. of benzene is 4.440°. What is the molecular weight of benzaldehyde in this solution? K_f for benzene is 5.12. *Ans.* 107.2.

9. A solution of 0.251 g. of acetone in 50 g. of glacial acetic acid gave a depression of the freezing-point of 0.339°. (*a*) What is the molal depression of the freezing-point for this solvent? (*b*) What is the molecular weight of a solute for which a solution of 0.249 g. in 18.64 g. acetic acid gave a freezing-point depression of 0.288°?

10. By dissolving 0.0821 g. of *m*-hydroxybenzaldehyde ($C_7H_6O_2$) in 20 g. of naphthalene (melting-point 80.1° C.) the freezing-point is lowered by 0.232° C. Assuming that the molecular weight of the solute is normal in the solution, calculate (*a*) the molal depression for naphthalene and (*b*) the heat of fusion per gram.
Ans. (*a*) 6.90°. (*b*) 35.9 cals. per gram.

11. Calculate the freezing-point of an aqueous solution of urea for which the mol fraction of urea is 0.0032, from the fact that the heat of fusion of water is 79.6 cal. per gram.

12. Calculate the osmotic pressure of 0.204 g. urea in 100 cc. of H_2O at 20°.
Ans. 0.817 atmos.

13. (*a*) What is the osmotic pressure at 27° of an aqueous solution containing 0.1 mol of urea in a liter of water? (*b*) What is the osmotic pressure of a benzene solution containing 0.1 mol per liter?

14. 34.2 g. of sugar (molecular weight = 342) is dissolved in 1000 g. of water. (*a*) What is the vapor pressure and (*b*) the osmotic pressure at 25°? (*c*) What is the freezing-point and (*d*) what is the boiling-point? The density of the solution is 1.03. The vapor pressure of water at 25° is 23.76 mm. The heat of vaporization of water is 536 cal. per gram and the heat of fusion is 79.6 cal. per gram.

15. The density of benzene at its melting-point is 0.8943, and its heat of fusion is 30.08 cal. per gram. The melting-point, 5.4°, is lowered 0.54° by the addition of phenol. (*a*) Calculate the osmotic pressure of the solution at 5.4° C. (*b*) Calculate the concentration of the solution.

Ans. (*a*) 2.14 atmospheres. (*b*) 9.91 g. per 1000 g. of benzene.

16. A concentrated solution of sugar at 25° has a vapor pressure of 23.45 mm., whereas pure water has a vapor pressure of 23.756 mm. What is the osmotic pressure of the solution? *Ans.* 17.66 atmos.

17. A concentrated, aqueous solution of sugar has an osmotic pressure of 100 atmospheres at 25°. What is the vapor pressure of this solution? The vapor pressure of pure water at this temperature is 23.756 mm.

18. Calculate the value of x in the table on p. 167. At 20° $p_0 = 17.535$ mm.

CHAPTER IX

SOLUTIONS OF ELECTROLYTES

Abnormal Solutes. As has already been pointed out, the acceptance of Avogadro's hypothesis was greatly retarded by the discovery of certain substances whose vapor densities were abnormal. Thus, the vapor density of ammonium chloride is approximately one-half of that required by the formula NH_4Cl, while the vapor density of acetic acid corresponds to a formula whose molecular weight is greater than that calculated from the formula, $C_2H_4O_2$. The anomalous behavior of ammonium chloride and kindred substances has been shown to be due, not to a failure of Avogadro's law, but to a breaking down of the molecules — a process known as *dissociation*. The abnormally large molecular weight of acetic acid, on the other hand, has been ascribed to a process of aggregation of the normal molecules, known as *association*. In extending the gas laws to dilute solutions similar phenomena have been encountered.

Association in Solution. When the molecular weight of acetic acid in benzene is determined by the freezing-point method, the depression of the freezing-point is abnormally small and consequently, the molecular weight will be greater than that corresponding to the formula, $C_2H_4O_2$. Acetic acid in benzene solution is thus shown to be associated. Almost all compounds containing the hydroxyl or cyanogen groups when dissolved in benzene are found to be associated. Solvents such as benzene and chloroform are frequently termed associating solvents, although in reality they exert no positive associating action. There is considerable experimental evidence to show that those substances whose molecules are associated in benzene and chloroform solution, are also associated in the free condition. Just as the depression of the freezing-point of a solution of an associated substance is abnormally small, so its osmotic pressure and other related properties are less than the calculated values.

Dissociation in Solution. Van't Hoff pointed out that the osmotic pressures of solutions of most salts, of all strong acids, and of all strong bases are much greater for all concentrations than would be expected from the osmotic pressures of solutions of substances like cane sugar or urea for corresponding concentrations. Although van't Hoff was unable to offer any satisfactory explanation of this anomaly, he showed

that the fundamental equation, $PV = RT$, would still hold, provided an empirical factor, i, were introduced and the equation written in the form,

$$PV = iRT. \tag{1}$$

It was originally believed that the factor, i, was a constant, but subsequently, when Arrhenius had advanced his theory of electrolytic dissociation, it became apparent that i must increase as the concentration diminishes. If the osmotic pressure of some substance, like cane sugar, which behaves normally, is represented by P_0, the factor i can be calculated by means of the expression,

$$i = \frac{P}{P_0}, \tag{2}$$

where P is the osmotic pressure of an abnormal solute at the same concentration. Since the osmotic pressure of a solution is proportional to the relative lowering of its vapor pressure Δp, to the elevation of its boiling-point ΔT_b, and to the lowering of its freezing-point ΔT_f, it follows that any one of these colligative properties may be similarly employed to calculate the value of the empirical factor, i, and

$$i = \frac{P}{P_0} = \frac{\Delta p}{(\Delta p)_0} = \frac{\Delta T_f}{(\Delta T_f)_0} = \frac{\Delta T_b}{(\Delta T_b)_0}, \tag{3}$$

where the subscript zero refers to the ideal solution. The vapor-pressure lowering, Δp, is equal to $p_{\text{solvent}} - p_{\text{solution}}$.

A more definite conception of the abnormal behavior of salts will be gained by an inspection of the following table giving the values of the molal freezing-point depressions $\Delta T_f/m$ of typical salts together with the corresponding values of i. The headings of the columns show the number of mols of solute dissolved in 1000 grams of water.

VALUES OF MOLAL FREEZING-POINT DEPRESSIONS*

Concentration (m)		0.005	0.006	0.01	0.02	0.05	0.1	0.2	0.5
KCl	$\Delta T_f/m$	3.648	3.640	3.610	3.564	3.502	3.451	3.394	3.314
	i	1.963	1.959	1.943	1.918	1.885	1.861	1.833	1.800
K_2SO_4	$\Delta T_f/m$	5.308	5.282	5.198	5.040	4.776	4.568	4.324	3.948
	i	2.857	2.843	2.798	2.713	2.570	2.459	2.333	2.316
$MgSO_4$	$\Delta T_f/m$	3.148	3.112	3.006	2.854	2.638	2.460	2.270	2.008
	i	1.694	1.675	1.618	1.536	1.420	1.324	1.223	1.084
$K_3Fe(CN)_6$	$\Delta T_f/m$	6.840	6.810	6.696	6.192	5.60	5.30	5.00	4.55
	i	3.681	3.665	3.604	3.333	3.02	2.86	2.70	2.45

* Noyes and Falk, J. Am. Chem. Soc., **32**, 1011 (1910).

As we have learned in the preceding chapter, the molal freezing-point depressions of dilute solutions of normal solutes is constant and, in the case of aqueous solutions, its value is 1.86°. Inspection of the preceding table reveals the fact that the values of the molal freezing-point depressions of the four salt solutions are all greater than those of solutions of normal solutes, such as cane sugar or mannitol. Furthermore, it will be seen that as the solutions are diluted, their molal depressions approach limiting values which are simple multiples of the normal depression, 1.86°. Thus, with solutions of KCl and $MgSO_4$, the molal depression approaches the value $3.72° = 2 \times 1.86°$, as the solutions are diluted, while with solutions of K_2SO_4 and $K_3Fe(CN)_6$ the respective limits toward which their molal depressions tend are $5.58° = 3 \times 1.86°$ and $7.44° = 4 \times 1.86°$. The preceding examples being typical of the behavior of all solutions in which the solute is an acid, a base or a salt, we may formulate the following generalization: — *The molal freezing-point depressions of dilute aqueous solutions of all abnormal solutes (acids, bases and salts) are greater than the corresponding depressions of solutions of normal solutes, and in every case, as the solutions are diluted, these depressions approach limiting values, which are simple multiples of the normal depression*, 1.86°.

These facts together with numerous other properties of dilute solutions of acids, bases and salts find their most satisfactory explanation in the theory of electrolytic dissociation.

The Theory of Electrolytic Dissociation. In 1887, Arrhenius* advanced an hypothesis to account for the abnormal osmotic activity of solutions of acids, bases and salts. He pointed out that just as the exceptional behavior of certain gases has been completely reconciled with the law of Avogadro, by assuming a dissociation of the vaporized molecule into two or more simpler molecules, so the enhanced osmotic pressure and the abnormally great freezing-point depressions of solutions of acids, bases and salts can be explained, if we assume a similar process of dissociation. He proposed, therefore, that aqueous solutions of acids, bases and salts be considered as dissociated, to a greater or less extent, into positively and negatively charged particles or *ions*, and that the increase in the number of dissolved units due to this dissociation is the cause of the enhanced osmotic activity. According to this hypothesis, hydrochloric acid, ammonium hydroxide and acetic acid, when dissolved in water, dissociate in the following manner: —

$$HCl \rightleftarrows H^+ + Cl^-$$
$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$
$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-.$$

* Z. physik. Chem., **1**, 631 (1887).

The reversed arrows indicate that a definite equilibrium exists between the ions and the undissociated molecules, a certain number of undissociated molecules always being present at finite concentrations. As the solution is diluted, the percentage of undissociated molecules steadily decreases, and ultimately, when the solution becomes infinitely dilute, the degree of dissociation approaches unity.

In each of the above cases, one molecule yields two ions, so that, if dissociation is complete, the maximum osmotic effect should not be greater than twice that produced by an equimolecular quantity of a substance which behaves normally. Reference to the preceding table shows that the value of i for potassium chloride approaches the limiting value of 2 as the solution is diluted. The other salts given in the table dissociate, according to Arrhenius, in the following manner: —

$$K_2SO_4 \rightleftarrows 2\,K^+ + SO_4^{--},$$
$$MgSO_4 \rightleftarrows Mg^{++} + SO_4^{--},$$
$$K_3Fe(CN)_6 \rightleftarrows 3\,K^+ + Fe(CN)_6^{---}$$

If these equations correctly represent the process of dissociation, then, when dissociation is complete, the osmotic effect of infinitely dilute solutions of potassium sulphate should be three times that produced by an equimolar concentration of a normal solute, and in the case of an infinitely dilute solution of potassium ferri-cyanide, the effect should be four times that of a normal solute. On referring to the table, it will be seen that the limiting values of i for each of the salts, KCl, K_2SO_4, $MgSO_4$ and $K_3Fe(CN)_6$, are 2, 3, 2 and 4, respectively.

According to the Arrhenius theory the term i represents the effective number of dissolved units, either molecules or ions, resulting from one molecule of solute. At low concentrations the ratio of ions to molecules is large, whereas at high concentration, where there are numerous collisions between ions, the number of molecules is relatively greater. Arrhenius calculated the extent of the dissociation into ions from the value of i, which can be determined experimentally by measuring the freezing-point depression or any of the colligative properties as given in equation (3).

Let us suppose that the degree of dissociation of 1 mol of a dissolved substance is α, each molecule yielding n ions. Then the number of undissociated mols will be $1 - \alpha$, and the total number of mols in the solution will be

$$1 - \alpha + n\alpha. \tag{4}$$

If ΔT_f is the depression of the freezing-point produced by the substance, and $(\Delta T_f)_0$ the depression produced by an equimolecular quan-

tity of an undissociated substance, then

$$\frac{1 - \alpha + n\alpha}{1} = \frac{\Delta T_f}{(\Delta T_f)_0} = i, \tag{5}$$

or

$$\alpha = \frac{i - 1}{n - 1}. \tag{6}$$

It will be observed that this formula is identical with that derived for the degree of dissociation of a gas (p. 21).

It was further pointed out by Arrhenius that all the substances which exhibit abnormal osmotic effects, when dissolved in water, yield solutions which conduct the electric current, whereas aqueous solutions of such substances as cane sugar, urea and alcohol exert normal osmotic pressures, but do not conduct electricity any better than the pure solvent. In other words, only electrolytes* are capable of undergoing ionic dissociation; hence Arrhenius termed the hypothesis the *electrolytic dissociation theory.*

As we have seen, when potassium chloride is dissolved in water, it is supposed to dissociate into positively charged potassium ions and negatively charged chloride ions. Accordingly when two platinum electrodes, one charged positively and the other negatively, are introduced into the solution, the potassium ions move toward the negative electrode and the chloride ions move toward the positive electrode, the passage of a current through the solution consisting in the ionic transfer of electric charges. Since the undissociated molecules are electrically neutral and hence do not participate in the transfer of electric charges, it follows that the conductance of a solution of an electrolyte is dependent upon the degree of dissociation. The relation between electrical conductance and the degree of ionization will be discussed in a subsequent chapter.

Properties of Completely Ionized Solutes. The chemical properties of an ion are very different from the properties of the corresponding atom or radical. For example, the sodium ion is present in an aqueous solution of sodium chloride, but there is no evidence of chemical reaction with the solvent; whereas, the element in the electrically neutral condition reacts violently with water, evolving hydrogen and forming a solution of sodium hydroxide. Chlorine in such compounds as $CHCl_3$, CCl_4, etc., is not precipitated by silver nitrate, since these compounds are not dissociated by water. Or chlorine may be present in a compound which is dissociated by water and yet not

* The term *electrolyte* strictly refers to the solution of an ionized substance, although it is often applied to acids, bases and salts because, when dissolved, they produce electrolytes.

exhibit its characteristic reactions, because it is present in a complex ion. Thus, potassium chlorate dissociates in the following manner: —

$$KClO_3 \rightleftarrows K^+ + ClO_3^-.$$

On adding silver nitrate, there is no precipitation, because the chlorine forms a complex ion with oxygen.

The physical properties of completely ionized solutions are, in general, additive. This is well illustrated by a series of solutions of colored salts, the color of which is due to the presence of a particular ion. It is found, when the solutions are sufficiently dilute to insure complete dissociation, that they all have the same color. The additive character of the colors of solutions of electrolytes is brought out in a striking manner by a comparison of their absorption spectra. Ostwald* photographed the absorption spectra of solutions of the permanganates of lithium, cadmium, ammonium, zinc, potassium, sodium, magnesium, hydrogen and aluminum, each solution containing 0.002 gram-equivalents of salt per liter. The absorption spectra are practically identical, the bands occupying the same position in each spectrum. This fact affords a strong confirmation of the theory of electrolytic dissociation, according to which a dilute solution is to be regarded as a mixture of electrically equivalent quantities of oppositely charged ions, each of which contributes its specific properties to the solution. The permanganate ion being colored, and common to all the salts examined, and the positive ions of the various substances being colorless, it follows that when dissociation is complete, the absorption spectra of all of the solutions must be identical.

The Theory of Complete Dissociation. The Arrhenius theory was satisfactory for many years and the degree of dissociation calculated from osmotic phenomena appeared to be in agreement with the degree of dissociation calculated from electrical conductance measurements. After the accumulation of a mass of exact experimental data, however, it became evident that the theory does not agree with all the experimental facts, particularly in the case of strong electrolytes like sodium or potassium chloride which have a high conductance. X-ray analysis indicated that even in the crystal lattice the potassium chloride exists in the form of ions and it seemed logical to believe that in dilute solutions there are no molecules of potassium chloride any more than there are in the crystal. From this point of view, salts and certain strong acids and bases may be regarded as completely dissociated and the degree of dissociation α, as calculated by Arrhenius, loses its significance for this type of solute. It might be expected then that the

* Z. physik. Chem., **9**, 579 (1892).

molal freezing-point depression of potassium chloride would be exactly twice the normal depression, not only at infinite dilution but at all moderate concentrations. The table on p. 194 shows, however, that it is smaller and that the molal depression becomes less as the concentration is increased. If this effect cannot be attributed to the formation of unionized molecules a new explanation is then necessary. We now have such an explanation in the *interionic attraction theory* of Debye and Hückel* based on electrodynamics, and it is so satisfactory from a theoretical standpoint and it agrees so well with the experimental facts of osmotic properties and electrical conductance that it is now accepted for strong electrolytes up to moderate concentrations. Details of the theory must be left to a later chapter (XVII), but it may be pointed out here that oppositely charged ions attract each other and cause deviations from the behavior of ideal solutions just as the attraction between molecules in a gas, corresponding to the a in van der Waals' equation, causes deviations from the behavior of an ideal gas. The properties of an imperfect gas approach those of an ideal gas at low pressures, and in the same way the properties of these electrolytes approach those of an ideal solute at low concentrations. In other words, the potassium and chloride ions are so far apart in very dilute solutions that they exert no attraction on each other, and the osmotic pressure is exactly twice as great as it is in the case of a non-electrolyte, such as sugar.

The different colligative properties are all related; a decrease in the osmotic pressure caused by interionic attraction must result in a corresponding decrease in the vapor-pressure lowering, freezing-point depression and boiling-point elevation. From a kinetic point of view the ions are non-volatile and block the surface of the solution and lower the vapor pressure by lessening the rate at which water molecules can escape. The interionic attraction tends to pull the ions at the surface away from the surface and lessen the retarding effect, i.e., to make the vapor-pressure decrease smaller than would be expected on the basis of the two ions. Accordingly the vapor-pressure lowering is less than would be expected if the ions acted independently, and the more concentrated the solution is, the closer are the ions and the greater is this inward attraction tending to lessen the influence on the vapor-pressure lowering and the other colligative properties of the solution.

It may be argued that there is no difference between partially attracted ions and the undissociated molecules of Arrhenius, but the point of view is entirely different and the interionic attraction theory has led to distinct advances in several independent fields. The the-

* Physik. Z., **24**, 185, 305 (1923); Ergeb. exact. Naturwiss., **III**, 199–276 (1924).

oretical advantages will become apparent in a later chapter. One of the advantages of the new theory is that it explains the different behavior of the various valence types — a phenomenon which could not be explained by the Arrhenius theory.

Classification of Electrolytes. Aside from a distinction between weak electrolytes, which are poor electrical conductors, and strong electrolytes which are good conductors, a distinction based on valences is useful. Thus, such substances as NaCl, KCl, KOH and HCl which yield on dissociation two singly charged ions are called uni-univalent electrolytes, while such substances as $CuSO_4$, $MgSO_4$ are called bi-bivalent electrolytes. In the same way, H_2SO_4 and Na_2CO_3 are uni-bivalent, $Ca(OH)_2$ and $BaCl_2$ are bi-univalent and $K_3Fe(CN)_6$ is uni-trivalent.

The total number of ions, n, is important, as already explained, in determining the factor by which the freezing-point depression or other colligative property must be multiplied in very dilute solutions. For NaCl, $n = 2$, for $CuSO_4$ 2, for $BaCl_2$ 3, for $K_3Fe(CN)_6$ 4, etc. In solutions of moderate concentration the multiplication factors are smaller than these numbers on account of the interionic attraction, and this attraction becomes greater as the number of charges on the ions increases. It is to be expected, then, that the high valence types will deviate more from the values obtained at infinite dilution than will the uni-univalent electrolytes — a fact which is abundantly verified by experiment.

The charges on the ions can be treated most successfully in terms of the *ionic strength*, a term which was first used by G. N. Lewis.* In calculating the ionic strength, μ, of a strong electrolyte the concentration of each ion (in gram-ions per 1000 grams of solvent) is multiplied by the square of its valence and all these quantities are added together and divided by 2.† The factor 2 is included because both positive and negative ions are involved. For example:

$$\text{for } 0.01\ m\ \text{NaCl}, \quad \mu = \frac{.01 \times 1^2 + .01 \times 1^2}{2} = 0.01;$$

$$\text{for } 0.01\ m\ CuSO_4, \quad \mu = \frac{.01 \times 2^2 + .01 \times 2^2}{2} = 0.04;$$

$$\text{for } 0.01\ m\ H_2SO_4, \quad \mu = \frac{.01 \times 1^2 + .01 \times 1^2 + .01 \times 2^2}{2} = 0.03.$$

* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 373.

† European physicists more often express concentrations on the volume basis rather than on the weight basis.

The ionic strength was found empirically by Lewis to simplify the calculations of solubility and other properties in mixed electrolytes, and its theoretical significance was later pointed out by Debye and Hückel.

Osmotic Properties of Electrolytes. In the Arrhenius theory the factor i is the ratio P/P_0 of the actual osmotic pressure to the ideal pressure of a non-dissociating solute; in the interionic attraction theory the factor g, called the osmotic coefficient, is defined as the ratio of the actual osmotic pressure to the ideal pressure which would exist if the solute were completely dissociated and no interionic attraction existed. Then

$$g = \frac{P}{\nu P_0}, \tag{7}$$

where ν is the number of ions into which a molecule dissociates ($\nu = 2$ in NaCl, $\nu = 3$ in $MgCl_2$, $\nu = 2$ in $MgSO_4$). Freezing-point depression, vapor-pressure lowering, or boiling-point elevation may be substituted for the osmotic pressure.

The Arrhenius theory centers attention on deviations from the behavior of unionized molecules and i is always greater than 1, whereas the interionic attraction theory centers attention on deviations from the behavior of completely ionized molecules and g is always less than 1.

In Fig. 75 the quantity, $1 - g$, is plotted against the concentration of ions, i.e., against νc, where c is the molal concentration of the solute. In very dilute solutions, where the interionic attraction is negligible, $P/\nu P_0$ becomes 1 and $1 - g$ becomes 0. Accordingly all the curves start from the origin.

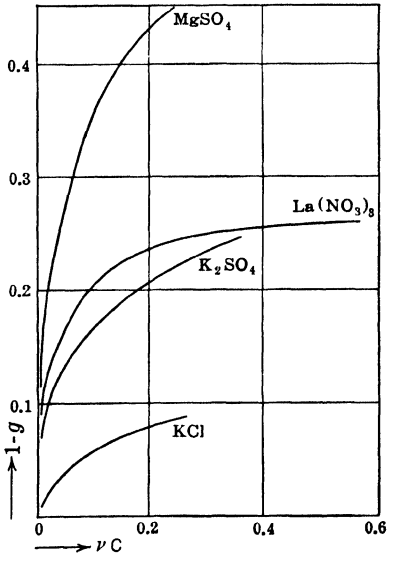


FIG. 75

It will be noted in a striking manner that $1 - g$, which measures the effect of interionic attraction, is greater the greater the valence. Magnesium sulphate, for example, gives a much greater departure, i.e., a smaller osmotic pressure, than potassium chloride, although both have the same concentration and the same number of ions. The theoretical reason will be discussed in a later chapter.

Concentrated Solutions. Thus far we have considered the behavior only of the solute and the electrical attraction of its ions. In concentrated solutions and in certain solvents other factors are involved. In actual practice the properties of the *solution* are measured rather than the properties of the isolated solute, and chemical reaction with the solvent or with other ions must be considered.

Many electrolytes exhibit a tendency to combine with other electrolytes in solution to form complex compounds. When these complex compounds dissociate, they give rise to *complex ions*. For example, if a solution of silver nitrate is treated with an excess of potassium cyanide, a reaction represented by the following equation occurs: —

$$2\,KCN + AgNO_3 = KNO_3 + KAg(CN)_2.$$

The resulting complex electrolyte dissociates according to the equation,

$$KAg(CN)_2 \rightleftarrows K^+ + Ag(CN)_2^-,$$

giving rise to the complex ion, $Ag(CN)_2^-$. Intermediate ions, also, may be formed as in the dissociation of calcium chloride. In very dilute solutions the reaction is

$$CaCl_2 = Ca^{++} + 2\,Cl^-$$

but in more concentrated solutions the reaction may be

$$CaCl_2 = CaCl^+ + Cl^-.$$

Particularly in the weak dibasic acids, like hydrogen sulphide, the first hydrogen atom ionizes much more readily than the second one.

There is ample evidence that many solutes combine with the water to form hydrates. The term *solvates* is more general, applying as it does to any solvent. Evidence for the existence of hydrates of cane sugar in aqueous solution has been furnished by Jones and Getman* from freezing-point data; by Scatchard† from calculations based on vapor-pressure measurements, and also by Philip‡ from measurements of the solubility of hydrogen in sucrose solutions. The average degree of hydration of sugar, as calculated by Scatchard from various available sources, is represented graphically in Fig. 76. The results obtained by each of the different methods appear to agree within the limits of their respective experimental errors and to confirm the existence of a definite hydrate of cane sugar in aqueous solution.

That the phenomenon of hydration is not confined to non-electro-

* Am. Chem. J., **32**, 327 (1904).
† J. Am. Chem. Soc., **43**, 2406 (1921).
‡ J. Chem. Soc., **99**, 711 (1907).

lytes has been shown by Jones and his students* who have measured the depression of the freezing-point of water produced by a large number of electrolytes in very concentrated solutions. Dissociation of electrolytes in aqueous solution increases with the dilution, becoming complete at a concentration of about 0.001 molal. We should expect the dissociation to diminish with increasing concentration, until, if the electrolyte is sufficiently soluble, the depression of the freezing-point becomes normal. Investigations by Jones and his co-workers† have shown that the facts are contradictory to this expectation. They found that the value of the molal depression of the freezing-point of water produced by a number of electrolytes diminishes with increasing

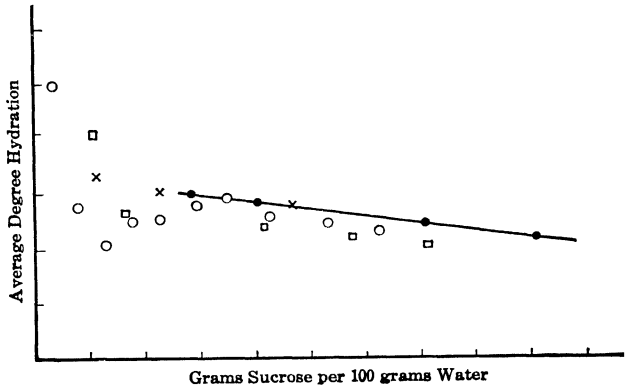


FIG. 76

concentration up to a certain point, as would be expected, and then increases again. This is illustrated by the freezing-point curves for several typical chlorides shown in Fig. 77. The increase in the molar depression becomes very marked at great concentrations; in fact, the molar depression in a molar solution is frequently greater than the molar depression corresponding to a completely dissociated salt. This phenomenon, which has been found to be quite general, may be accounted for by assuming that the dissolved substance has entered into combination with a portion of the water, thus removing it from the rôle of solvent. A molecular complex formed by the union of 1 molecule of solute and a number of molecules of water will act as a single dissolved unit in depressing the freezing-point of the pure solvent. Evidently the total amount of water present which functions as solvent will be

* Publ. No. **60**, Carnegie Institution.

† Am. Chem. J., **22**, 5, 110 (1899); **23**, 89 (1900).

diminished by the amount of water which has been appropriated by the solute.

If hydrates exist in aqueous solution, then those solutes which exhibit the greatest abnormal action on the freezing-point of water should be the ones which crystallize from the solution with the greatest amount of water of crystallization. That there is a relation between

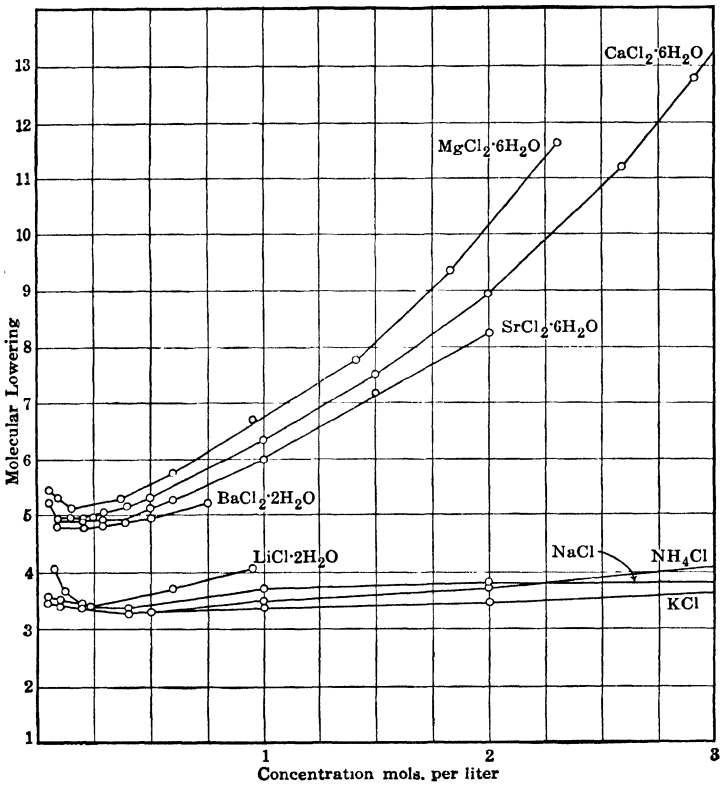


FIG. 77

freezing-point depression and water of crystallization is shown by the curves in Fig. 77. Those salts which crystallize without water of crystallization produce the least depression of the freezing-point. Those crystallizing with two molecules of water are next in order, and then follow those crystallizing with four and six molecules respectively. Similar relations are found to hold for the corresponding bromides, iodides and nitrates. We conclude, therefore, that, in concentrated solutions, those solutes which crystallize with the same amount of

water produce approximately the same depression of the freezing-point of water.

Additional evidence for the hydration of ions is given in Chapter XV. It is a matter of common observation also that the emission spectra of excited gases contain sharp lines but that the absorption spectra of solutions usually do not contain fine lines. Hydration of the absorbing ions is thought to give a greater variation in the possible energy states and cause a blurring out of these lines. In a few cases, however, as in certain rare earth salts and dilute potassium permanganate it is possible to obtain line structure, and in the latter case it is probable that the ions are not appreciably hydrated.

It must be emphasized that hydration is only *one* of the factors which cause deviations from the laws of ideal solutions.

Summary. It may be concluded from what has been said in this chapter that solutions of electrolytes may be classified roughly into four different groups depending on the concentration.

In exceedingly dilute solutions (less than 0.0001 M for strong electrolytes and much less for weak electrolytes) the solute is completely dissociated, in agreement with either the Arrhenius or the interionic attraction theory.

In dilute solutions (0.0001 to .01 M) the Arrhenius theory is satisfactory only for weak electrolytes such as acetic acid, and the theory of interionic attraction is necessary and adequate for strong electrolytes.

In solutions of moderate concentration (0.01 M to 1 M) the properties of strong electrolytes are affected both by interionic attraction and by the presence of unionized molecules. The mere fact that one can smell hydrochloric acid molecules from a 1 M solution of HCl proves that some undissociated molecules exist in the solution. Exact theoretical calculations cannot yet be made in this region.

In concentrated solutions (greater than 1 M) the character of the solvent is markedly changed by the presence of the solute and the situation is very complicated. Hydration or solvation of the solute and depolymerization of the solvent may be factors.

These classifications are to be taken only as rough approximations, and they vary greatly for different electrolytes. Apparently some salts, such as mercuric chloride and cadmium chloride, are only partly dissociated even in dilute solution. It is hoped that new investigations of crystal structure and of optical measurements will lead to a better understanding of these electrolytes.

REFERENCES

The Ionization Theory. Symposium Faraday Society. Trans. Faraday Soc. **15**, 1–178 (1919); **23**, 334 (1927).

Strong Electrolytes. Hückel. Ergeb. exact. Naturwiss., III, 199–276 (1924).

The Conductivity of Solutions and the Modern Dissociation Theory. Davies.

PROBLEMS*

1. Dichloracetic acid is among those acids which lie intermediate between weak and strong acids. Aqueous solutions of strength (*a*) 0.1 *m* and (*b*) 0.01 *m* have freezing-points of −0.278° and −0.033° respectively. On the basis of the Arrhenius theory, what is the degree of ionization in each of these solutions?

Ans. (*a*) 50 per cent. (*b*) 77 per cent.

2. A 0.1 molal solution of fumaric acid in water freezes at −0.204°. Assuming that only one of the acid groups is ionized to an appreciable extent at this concentration, what is the degree of dissociation of the acid?

3. A 0.08 *m* solution of chloracetic acid is 13 per cent ionized. Calculate (*a*) the freezing-point, (*b*) boiling-point, and (*c*) the vapor pressure at 25° of this solution. The vapor pressure of water at 25° is 23.756 mm.

Ans. (*a*) −0.168°. (*b*) 100.047°. (*c*) 23.714 mm.

4. A certain monobasic acid is 10 per cent dissociated in 0.01 *m* solution. Calculate (*a*) freezing-point, (*b*) boiling-point, (*c*) vapor pressure at 25°, (*d*) osmotic pressure.

5. A solution containing 1.5 g. KCl in 100 g. H_2O freezes at −0.684°. What is the value of *i*? What is the vapor pressure of this solution at 25°? The vapor pressure of water is 23.756 mm. *Ans.* 23.599 mm.

6. Express *g* in terms of freezing-point depression, boiling-point elevation, and vapor-pressure lowering. (*a*) What is the value of *g* for a solution of potassium chloride in 100 g. of water which freezes at −0.684° (preceding problem)? (*b*) Using *g* calculate the vapor pressure at 25° of this solution.

Ans. (*a*) 0.916. (*b*) 23.599.

7. A solution of 7.67 g. of Na_2SO_4 in 1000 g H_2O was found to produce the same lowering of the vapor pressure as an 0.134 *m* solution of urea. What is the value of the osmotic coefficient, *g*? Urea does not dissociate.

8. A 0.2 *m* solution of $MgSO_4$ has a vapor pressure of 23.660 at 25° (H_2O = 23.756). Calculate the values of (*a*) *g*, (*b*) ΔT_f, (*c*) ΔT_b and (*d*) the osmotic pressure. *Ans.* (*a*) 0.563. (*b*) −0.418. (*c*) 0.117°. (*d*) 5.05 atmospheres.

9. A 0.5 *m* solution of KCl freezes at −1.657°. (*a*) What is the value of the osmotic coefficient, *g*? (*b*) What is the boiling-point?

10. The vapor pressure of water at 0° is 4.620 mm. The lowering of the vapor pressure produced by dissolving 5.64 g. of sodium chloride in 100 g. of water is 0.142 mm. What is the freezing-point of the solution? *Ans.* −3.216°.

11. A 0.5 *m* solution of $Al_2(SO_4)_3$ boils at 100.585°. What is the freezing-point of the solution?

12. For a 0.01 *m* solution of a certain electrolyte $g = 0.901$ and $\Delta T_f = 0.067$. A 0.02 *m* solution of this electrolyte freezes at −0.124°. What is the value of *g* for the 0.02 *m* solution? *Ans.* 0.836.

13. 0.1 *m* solutions of $MgCl_2$ and $CdCl_2$ freeze at −0.494° and −0.384° respectively. What is the osmotic coefficient of each?

* The concentrations *m* in these problems refer to mols per 1000 g. of water.

14. From the following tables of freezing-points calculate g and plot $1 - g$ against νc.

NaCl		$K_4Fe(CN)_6$	
c	$\Delta T_f/m$	c	$\Delta T_f/m$
0.01	3.604	0.0075	6.9
0.04	3.53	0.025	6.17
0.2	3.424	0.075	5.41
0.7	3.36	0.191	4.80

15. What is the ionic strength of 0.02 m solutions of each of the following substances: (*a*) LiCl, (*b*) K_2SO_4, (*c*) $MgSO_4$, (*d*) Na_3PO_4, (*e*) $K_4Fe(CN)_6$?

Ans. (*a*) 0.02. (*d*) 0.12.

16. A solution of sodium chloride has an ionic strength of 0.24. (*a*) What is its concentration? (*b*) What concentration of Na_2SO_4 would have the same ionic strength? (*c*) What concentration of $MgSO_4$?

17. A molal solution of sucrose freezes at $-2.06°$. Assuming that any abnormality is due to hydration of the sugar, how many mols of water are removed from the rôle of solvent per mol of sucrose.

18. If the precision obtainable in determining the lowering of the freezing-point is 0.001°, the elevation of the boiling-point is 0.0015° and the lowering of vapor pressure is 0.001 mm., to what (per cent) error would the degree of dissociation α of 0.08 m chloracetic acid be subjected when determined from experimental measurements of these quantities? (Problem 3.)

CHAPTER X

COLLOIDS

Crystalloids and Colloids. In the course of his investigations on diffusion in solutions, Thomas Graham* drew a distinction between two classes of solutes, which he termed *crystalloids* and *colloids*. Crystalloids, as the name implies, can be obtained in the crystalline form: to this class belong nearly all of the acids, bases and salts. Colloids, on the other hand, are generally amorphous, such substances as albumin, starch and caramel being typical of the class. Because of the gelatinous character of many of the substances belonging to this class, Graham termed them colloids (κόλλα = glue, and εἶδος = form). The differences between the two classes are most apparent in the physical properties of their solutions. Crystalloids diffuse much more rapidly than colloids; thus, the velocity of diffusion of caramel is nearly 100 times slower than that of hydrochloric acid at the same temperature. Whereas crystalloids exert osmotic pressure, lower the vapor pressure and depress the freezing-point of the solvent, colloids have very little effect upon these properties.

The terms crystalloid and colloid, as used at the present time, have acquired different meanings from those assigned to them by Graham. The terms are now considered to refer, not so much to different classes of substances, as to different states of subdivision.

Disperse Systems. If in a two-component system, the size of the particles of one of the components is gradually reduced until its dimensions become microscopic or submicroscopic, we have what is known as a *disperse system*. The characteristic properties of disperse systems are attributable to the enormous surface of the dispersed phase. If a cube of gold 1 cm. on an edge, having a total surface of 6 sq. cm., is cut in half in the three directions, there will be 8 cubes having edges of 0.5 cm. and the surface will be $8 \times 6 \times 0.5^2$ or 12 sq. cm. If cut into 1000 cubes 1 mm. on an edge, the total surfaces will be 60 sq. cm. The surface area will be increased to 60,000 sq. cm., or 6 sq. m., if the cubes are 1 μ† on an edge. If the cubes are 1 $m\mu$‡ on an edge there will be 10^{21} cubes, and the area will be 6000 sq. m. or $1\frac{1}{2}$ acre. It is obvious that surface effects which are undetected on material

* Trans. Roy. Soc., **151**, 183 (1861).

† 1 μ = 1 micron = 0.001 mm. ‡ 1 $m\mu$ = 0.001 μ.

having an area of 6 sq. cm. may become very pronounced when the material is dispersed to give a total surface of several square meters.

One of the most important results of this large surface is the adsorption of material by the particles. This adsorption may lead to the formation of an electrical "double layer," or atmosphere, around the particles which prevents them from collecting into larger aggregates.

If the particles are large, they have essentially the properties of ordinary material, whereas if they are very small they are indistinguishable from true solutions. Between these two regions we have the colloidal state, in which the particles are small enough to have great surface area but large enough so that the solution is not strictly homogeneous and the presence of discrete particles can be detected with the ultramicroscope. It follows, therefore, that the size of the dispersed particles determines whether or not a system is to be considered as colloidal. At one extreme we have true solutions in which no lack of homogeneity can be detected, even by the ultramicroscope, and at the other extreme we have coarse-grained suspensions in which the particles are visible to the naked eye. Between these two limits all possible degrees of subdivision are possible, and it is a very difficult matter to draw sharp lines of distinction between true solutions and colloid solutions on the one hand, and between colloids and suspensions on the other. It is arbitrarily considered that particles with diameters between 1 $m\mu$ and 100 $m\mu$ (10^{-7} and 10^{-5} cm.) are colloids. These relations are summarized in the accompanying table.

Classification of Particles According to Size

Coarse dispersions (suspensions, emulsions, etc.):
Magnitude of particles greater than 0.1 μ.
Colloid solutions:
Magnitude of particles between 0.1 μ and 1 $m\mu$.
Molecular and ionic dispersoids. True solutions:
Magnitude of particles about 1 $m\mu$ and smaller.

Nomenclature. Aside from the general definition of the colloid state, i.e., particles from 1 to 100 $m\mu$ in size, there are other points of distinction. Graham distinguished between a *sol*, in which the colloidal system resembles a liquid, and a *gel*, in which it resembles a solid or jelly-like substance. *Hydrosol* and *hydrogel* are terms applied to colloid systems having water as one component.

In the reversible transformation of a sol into a gel, we are not warranted in referring to the change from gel to sol as an act of solution, for if the gel really dissolved, a solution and not a sol would result. The reversible transformations are termed *gelation* and *solation*, the

former designating the formation of a gel from a sol and the latter the reverse process.

When the dispersion is not too great, colloidal solutions may be divided into *suspensions* and *emulsions*, depending on whether the disperse phase is a solid or a liquid. As the dispersion is increased, we obtain suspension and emulsion colloids, which may be conveniently called *suspensoids* and *emulsoids*.* Suspensoids and emulsoids are included under the general term, *dispersoids*. The classification of sols as suspensoids and emulsoids, however, is not entirely satisfactory. A better system is that in which the presence, or the absence, of affinity between the disperse phase and the dispersion medium is made the basis of classification. Where there is marked affinity between the two phases, the system is termed *lyophile*, and where such affinity is absent, the system is termed *lyophobe*. When the dispersion medium is water, the terms *hydrophile* and *hydrophobe* are employed.

The Ultramicroscope. When a narrow beam of sunlight is admitted into a darkened room, the dust particles in its path are rendered visible by the scattering of the light at the surface of the particles. If the air of the room is free from dust, no shining particles will be seen and the space is said to be "optically void." When the particles of dust are very minute, the beam of light acquires a bluish tint.

The luminosity of the path of a beam of light is known as the *Tyndall phenomenon* and may be considered as an indication of the presence of suspended particles, provided the luminosity is not caused by fluorescence. Almost all colloid solutions exhibit this phenomenon when a powerful beam of light is passed through them, thus proving the presence of discrete particles in the solutions.

The ultramicroscope is an instrument devised by Siedentopf and Zsigmondy† for the detection of colloid particles much too small to be seen with a microscope. A powerful beam of light, issuing from a horizontal slit, is brought to a focus within the colloidal solution under examination by means of a microscope objective, and this image is viewed through a second microscope, the axis of which is at right angles to the path of the beam. When examined in this way a colloid solution usually appears to be swarming with minute particles moving rapidly in a dark field, whereas a true solution if properly prepared appears optically void.

A diagram of the ultramicroscope is shown in Fig. 78. It is necessary to view the particles by reflected light rather than by transmitted light because the colloidal particles are smaller than the wave-length

* Kruyt uses these terms in a different sense.

† Zsigmondy, "Colloids and the Ultramicroscope." Translated by Alexander.

of visible light. The intensity of the light rather than the magnifying power of the microscope is the limiting factor in detecting the smallest colloid particles with the ultramicroscope. It is possible to extend the lower limit of detection by using shorter wave-lengths, i.e., ultra-violet light, with quartz lenses and photographic plates. It should be emphasized that the apparent size of the bright image bears no relation to the size of the particle. It is, however, possible to count the number of particles in a given volume. By means of a chemical analysis, the mass of colloid per unit of volume can be determined, and from this, the average mass of each particle can be calculated. If the particles are assumed to be spherical in shape and to have the same density as larger masses of the same substance, we can calculate the volume of a single particle, and from this its diameter. Thus, Burton* in his experiments on gold, silver and platinum sols, found the average diameter of the colloidal particles to range from 200 to 600 $m\mu$. Later experiments have shown that it is possible to detect gold particles as small as 5 $m\mu$ in diameter.

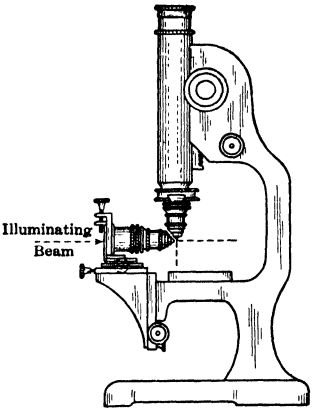


FIG. 78

The ultramicroscopic character of lyophile sols is by no means sharply defined, notwithstanding the fact that they exhibit the Tyndall phenomenon. It has been suggested by Zsigmondy that the lack of sharpness in definition observed in this case is probably due to the relatively small difference between the refractive indices of the disperse phase and the dispersion medium. Where the difference between the refractive indices of the two phases is very great, as in the case of the metallic sols, excellent definition is obtained.

Ultrafiltration. Almost all sols can be filtered through ordinary filter paper without undergoing more than a slight change in concentration. The rate of filtration varies widely depending on the viscosity of the sol. As a general rule lyophile sols filter more slowly than lyophobe sols owing to the high viscosity of the former. By employing a series of porous plates having different degrees of porosity it is possible to estimate the size of the particles which constitute the disperse phase in certain sols. Such measurements have not been successfully applied to particles less than about 40 $m\mu$ in diameter.

If we make use of a series of graduated filters prepared by impreg-

* Phil. Mag., **11**, 425 (1906).

nating filter paper with a solution of collodion in acetic acid, it is not only possible to separate suspensoids from their dispersion media but also to effect the concentration of emulsoids. Ultrafiltration is an exceedingly complex process, involving electrical attraction and adsorption as well as the ordinary process of mechanical separation. For example, if we attempt to filter a ferric hydroxide hydrosol the filter becomes negatively charged in contact with the water, and on the entrance of the positively charged sol into the pores of the filter the colloid is immediately discharged and the disperse phase precipitated. After the pores of the filter become partially stopped with particles of the colloid, the sol will then pass through very slowly.

Ultrafilters are useful in removing impurities from sols, and they find extensive application in bacteriology. Bacteria can generally be removed from solutions by ultrafilters, but certain diseases such as infantile paralysis and the mosaic disease of tobacco plants are connected with "filterable viruses" which pass through the finest ultra filters.

The Brownian Movement. If a liquid in which fine particles of matter are suspended, such as an aqueous suspension of gamboge, is examined under the microscope, the suspended particles will be seen to be in a state of ceaseless, erratic motion. This phenomenon, which had frequently been observed, was first correctly interpreted in 1827, by the English botanist, Robert Brown, while examining a suspension of pollen grains. It is commonly known as the *Brownian movement.* Brown stated that "the movements arose neither from currents in the fluid nor from its gradual evaporation; but belonged to the particle itself."

In 1863 Wiener suggested that the cause of the phenomenon was the actual bombardment of the suspended particles by the molecules of the suspending medium. Twenty-five years later, a similar conclusion was reached independently by Gouy, who showed that neither light, nor convection currents within the liquid, could possibly give rise to the motion. Furthermore, Gouy showed the movement to be independent of external vibration, and only slightly influenced by the nature of the suspended particles. The smaller the particles and the less viscous the suspending medium, the more rapid the motion was found to be. By far the most striking feature of the phenomenon, however, is the fact that the motion is ceaseless. Deposits have been found in which the Brownian movement has apparently been going on undisturbed through geologic ages.

The first quantitative investigation of the Brownian movement was undertaken by Svedberg in 1906. In 1909, Perrin undertook the study of sedimentation equilibrium, which he inferred must be de-

pendent upon the Brownian movement. The results of his investigation are here briefly summarized.

Perrin's Experiments. It has been shown (p. 24), that the mean kinetic energy of 1 mol of a perfect gas is equal to $3/2\ pv$, and since $pv = RT$, we may write

$$E_k = \frac{3}{2}\frac{RT}{N}, \tag{1}$$

where E_k is the mean kinetic energy of one particle and N is the Avogadro constant, i.e., the number of molecules in a gram-molecule. It is evident that, if E_k can be measured, equation (1) affords a means of calculating N, provided we are warranted in applying an equation which has been derived for the gaseous state to a suspension of fine particles in a liquid medium. It has already been shown that the simple gas laws hold for dilute solutions, and we may assume that, at the same temperature, the mean kinetic energy of the dissolved molecules is equal to that of the gaseous molecules. In other words, at the same temperature, the mean kinetic energy of the molecules of all fluids is the same, and is directly proportional to the absolute temperature. Since the gas laws apply equally well to dilute solutions, containing either large or small molecules, Perrin held that there was no *a priori* reason for assuming that the particles of a suspension should not conform to the same laws. If this assumption is correct, the grains of a pollen suspension should so distribute themselves under the influence of gravity that, when equilibrium is attained, the lower layers will have a higher concentration than the upper layers. In other words, the distribution should be strictly analogous to the distribution of the air over the surface of the earth, the density being greatest at the surface and diminishing as the altitude increases.

Let us imagine a suspension to be confined within a vertical cylinder whose cross-sectional area is s sq. cm. Assuming that the suspension has come to equilibrium under the influence of gravitation, let n be the number of grains per unit of volume, at a height h from the base of the cylinder. Since the concentration diminishes as the height increases, the number of grains at a height, $h + dh$, will be $n - dn$. The pressure of the grains at the height h will be $\frac{2}{3}\ nE_k$, since $nE_k = \frac{3}{2}\ pv$. In like manner, the pressure at the height, $h + dh$, will be $\frac{2}{3}\ (n - dn)E_k$. The difference in pressure between the two levels is $-\frac{2}{3}\ E_k\ dn$ and, since the pressure acts over a surface of s sq. cm., the difference of diffusive forces acting over the cross-sectional area of the cylinder is $-\frac{2}{3}\ sE_k\ dn$. Since the system is in equilibrium, this difference in pressure must be balanced by the difference in the effect of gravitation at

the two levels. Let ϕ be the volume of a single grain, D its density, and δ the density of the suspending medium. The resultant downward pull upon a single grain will be $\phi\ (D - \delta)g$, where g is the acceleration due to gravity. The volume of liquid between the two levels being $s\ dh$, it follows that the total downward pull upon all the grains included between the two levels must be $ns\phi\ (D - \delta)g\ dh$. It is this force which opposes the tendency of the grains to distribute themselves uniformly throughout the entire volume of the suspending medium, or, in other words, it is the force which acts in opposition to the diffusive force, $-\frac{2}{3}\ s\ dnE_k$. When equilibrium is established, these two forces must be equal, and we may then write

$$-\tfrac{2}{3}\ sE_k\ dn = ns\phi\ (D - \delta)g\ dh. \tag{2}$$

If n_0 and n denote the number of grains per unit of volume at each of two planes, h units apart, we obtain, on integrating equation (2),

$$\tfrac{2}{3}\ E_k\ \ln\ n_0/n = \phi\ (D - \delta)gh. \tag{3}$$

On substituting in equation (3), the value of E_k in equation (1), and transforming to Briggsian logarithms, we have

$$2.303\ RT/N\ \log\ n_0/n = \tfrac{4}{3}\ \pi r^3 g(D - \delta)h, \tag{4}$$

ϕ being expressed in terms of the mean radius, r, of a single grain. It is evident that if we can measure n, n_0, D, δ, and r in equation (4), the calculation of the Avogadro constant, N, becomes possible, assuming that any effect due to electrical charges is negligible.

The determination of the density of the grains, D, was carried out in two different ways with suspensions of gamboge and mastic which had been rendered uniform by a process of fractional centrifuging. In the first method, the grains were dried to constant weight at 110°, and then, by heating to a higher temperature, a viscous liquid was obtained which, on cooling, formed a glassy solid. The density of this solid was determined by suspending it in a solution of potassium bromide of known density. In the second method the density was calculated from the difference between the density of the suspension and the density of the water.

A microscope furnished with suitable micrometers was employed in the determination of n and n_0. The whole cell was only 0.1 mm. in height. By focusing the microscope at different depths, the average number of grains in the field of view, at each level, was counted. Perrin was able to photograph the larger grains at different levels, whereas, with the smaller grains, it was necessary to reduce the field so that relatively few grains were visible. The average number of grains counted at any two different levels gave the desired ratio, n_0/n.

The only other quantity in equation (4) to be measured is the average radius of the grains, r. To determine this quantity, Perrin made use of Stokes' formula, according to which the force required to impart a uniform velocity v to a particle of radius r, moving through a liquid medium whose viscosity is η, is given by the formula $6\pi\eta rv$. From the rate at which a suspension clears under the influence of gravity the value of r can be calculated. This value was checked very satisfactorily by counting the number of particles and weighing the total mass after precipitation.

Five series of experiments carried out by Perrin with gamboge suspensions in which several thousand individual grains were counted, gave as a mean value of N, in equation (4), 6.9×10^{23}. Similar experiments with mastic suspensions gave $N = 7.0 \times 10^{23}$. Nordlund* later repeated Perrin's experiments, employing a colloidal solution of mercury, and an arrangement of apparatus whereby the movements of the particles could be recorded photographically. The mean value of N, derived from twelve carefully executed experiments, was 5.9×10^{23}, the average deviation of the results of the individual experiments from the mean being approximately 10 per cent.

The Brownian movement in gases has been studied by Millikan,† and also by Fletcher,‡ employing a minute drop of oil as the suspended particle. In the gaseous state, where the intermolecular distances are greater than in the liquid state, not only are the collisions less frequent, but the mean free paths are appreciably longer. These conditions are favorable to the study of the Brownian movement, and offer an opportunity for the determination of the Avogadro constant with a high degree of accuracy. As the mean of nearly six thousand measurements, Fletcher gives $N = 6.03 \times 10^{23}$, this value being accurate to within 1.2 per cent.

These values are in close agreement with the values of the Avogadro number given on p. 5, a fact which strengthens both the kinetic theory of gases and the assumption that these comparatively large particles behave as individual molecules in a gas.§

Displacement of Particles. The actual movements of the individual grains of a suspension when observed under the microscope are seen to be exceedingly complex and erratic. The horizontal projections of the paths of three different grains in a suspension of mastic are shown in Fig. 79, the dots representing the successive positions

* Z. physik. Chem., **87**, 60 (1914).

† Phys. Rev., **1**, 220 (1913).

‡ Phys. Rev., **4**, 453 (1914).

§ The matter is more fully discussed by Westgren, Z. physik. Chem., **89**, 63 (1914).

occupied by the particles after intervals of 30 seconds. The straight line joining the initial and final positions of a particle for a given time interval is called the *horizontal displacement* of the particle.

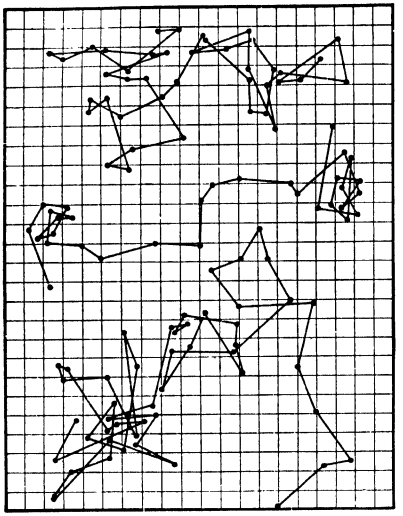


FIG. 79

If the time taken by the particle to move from its initial to its final position be t, Einstein* has shown that the mean value of the square of the X component of the horizontal displacement of a spherical particle of radius r, ought to be

$$X^2 = \frac{RT}{N}\frac{t}{3\pi r\eta}, \qquad (5)$$

where η is the viscosity of the suspension medium, and where the other symbols have their usual significance.

This equation was tested by Perrin, using suspensions of gamboge and mastic. Some of the results obtained are given in the following table:—

VALUES OF N CALCULATED BY EINSTEIN'S EQUATION

Suspension	r in $m\mu$	$m\times10^{15}$	No. of displacements	$N\times10^{-23}$
Gamboge in water	367	246	1500	6.9
Gamboge in 10% solution of glycerine	385	290	100	6.4
Mastic in water	520	650	1000	7.3
Mastic in 27% solution of urea	5500	750,000	100	7.8

It will be seen, that notwithstanding the large variations in the granular masses, m, of the different suspensions recorded in the table, the values of N, calculated by means of Einstein's equation, are quite concordant. Perrin gives as the mean value of all of his experiments, $N = 6.85 \times 10^{23}$.

Physical Properties of Colloid Solutions. There is a great difference in many physical properties between the lyophobe colloids and the lyophile colloids. Since there is no particular attraction between the

* Z. Elektrochem., **14**, 235 (1908).

colloid particles and the suspension medium in lyophobe colloids, the physical properties are additive. Because the relative volume of the colloid phase is very small, the properties of the colloid system are nearly the same as those of the dispersion medium. In lyophilic colloids the force of attraction between the disperse phase and the dispersion medium may lead to properties which differ greatly from those of the dispersion medium.

It was shown by Linder and Picton* that the density of lyophobe sols follows the law of mixtures. This is clearly shown by the following table, in which are given the observed and calculated values of the density of a series of arsenious sulphide sols.

DENSITY OF ARSENIOUS SULPHIDE SOLS

As_2S_3 (grams per liter)	Density (obs.)	Density (calc.)
44	1.033810	1.033810
22	1.016880	1.016905
11	1.008435	1.008440
2 45	1.002110	1.002100
0.1719	1.000137	1.000134

The density of lyophile sols, on the other hand, cannot be calculated from the composition of the sol. This fact may be taken as evidence in favor of the view that a closer relation exists between the disperse phase and the dispersion medium in lyophile than in lyophobe sols.

The viscosity of lyophobe colloids is nearly the same as that of the dispersion medium but sometimes it is slightly greater.

VISCOSITY OF LYOPHILE SOLS

Sol.	Temp. 20° Concentration	Viscosity
Gelatine.....	1	0.021
Gelatine.....	2	0.037
Silicic acid.....	0.81	0.012
Silicic acid.....	0.99	0.016
Silicic acid.....	1.96	0.032
Silicic acid	3.67	0.165

On the other hand, the viscosity of lyophile sols is frequently much greater than that of the pure dispersion medium. The viscosity of

* J. Chem. Soc., **67**, 71 (1895).

lyophile sols also increases with increasing concentration, as is shown by the data of the preceding table.

The surface tension of lyophobe sols has been shown by Linder and Picton to be practically identical with that of the dispersion medium.

Weight of Colloid Particles. If the weight of a single colloid particle is regarded as its molecular weight, it is obvious that the molecular weights of colloids must be enormous. Colloid particles range in diameter from 1 $m\mu$ to 100 $m\mu$; the diameter of atoms is of the order of 0.1 $m\mu$. In a colloid system the particles are not all uniform in size and any measurement of their weight must be considered as an average weight. It is perhaps better to speak of particle weight rather than molecular weight.

The ordinary methods for determining molecular weights in solution are beset with difficulties when applied to colloid systems because it is almost impossible to wash out all the ions, and each ion is just as effective as a colloid particle in lowering the vapor pressure or the freezing-point, or creating an osmotic pressure. Furthermore, the effect to be measured is very small. It will be remembered that 6×10^{23} molecules dissolved in a liter of water will lower the freezing-point 1.86°, and if ten thousand of these units are combined into one colloid particle the freezing-point lowering will be only 0.000186° — and a mere trace of electrolyte left behind will produce an effect greater than this.

A few satisfactory measurements appear to have been made using collodion membranes and measuring the apparent osmotic pressure of concentrated solutions under conditions where ions would not affect the pressure. Sörensen found a molecular weight of 34,000 for egg albumin, and Adair* obtained 67,000 for hemoglobin.

The particle size may be determined also through measurements of the rate of settling and the application of Stokes' law. These sedimentation studies have been valuable in determining the size and distribution of size among large particles.

Unquestionably the most important work on the particle weight of colloids has been done by Svedberg with the ultracentrifuge. The rate of settling of small colloid particles under the force of gravity is too slow to permit accurate measurements, but with Svedberg's apparatus it is possible to obtain a force 100,000 times as great as that of gravitation. The colloidal material is placed in a glass tube set like a spoke in a wheel and whirled at a rate of 40,000 revolutions per minute and the rate of migration of the particles is determined by photographing, at intervals, the edge of the colloid material as it moves out

* Proc. Roy. Soc., **A 109**, 292 (1925).

from the center. Some of the results obtained with Svedberg's methods are given in the following table.*

Protein	Particle Weight
Egg albumin	34,500
Hemoglobin	68,100
Serum albumin	67,500
Serum globulin	103,600
Phycocyan	105,500
Phycoerythin	208,000
Limulus-hemocyanin	1,760,000

Cataphoresis. One of the most characteristic features of colloidal systems is the existence of positive or negative electrical charges on the colloid particles which lead to a "double layer" of oppositely charged ions, or ionic atmosphere. The existence of these charges may be very easily proved by placing the particles in an electrostatic field and observing the migration to the negative or positive pole. This phenomenon is called cataphoresis and was first observed by Reuss in 1807, and later by Linder and Picton.† They showed that, when the terminals of an electric battery are connected to two platinum electrodes dipping into a colloidal solution of arsenious sulphide, there is a gradual migration of the colloid to the positive pole. A similar experiment with a solution of colloidal ferric hydroxide resulted in the transport of the dissolved colloid to the negative pole. It follows, therefore, that the particles of colloidal arsenious sulphide are negatively charged, while those of colloidal ferric hydroxide carry a positive charge. It has been found that most colloids are electrically charged. In the following table some typical colloids are classified according to the character of their electrification in aqueous solution.

ELECTRICAL CHARGES OF HYDROSOLS

Electro-positive	Electro-negative
Metallic hydroxides	All the metals
Methyl violet	Metallic sulphides
Methylene blue	Aniline blue
Magdala red	Indigo
Bismarck brown	Eosine
Hemoglobin	Starch

* Svedberg, " Colloid Chemistry," p. 164.

† J. Chem. Soc., **61**, 148 (1892).

The nature of the charge varies with the dispersion medium used, some colloidal solutions in turpentine, for example, having charges opposite to those in water.

Direct measurements of the velocity with which the particles move in cataphoresis have been made by Cotton and Mouton.* By observing with a microscope the distance over which a single particle traveled in a given interval of time, under a definite potential gradient, they calculated the average velocity of migration of a number of lyophobe sols. The following table gives the velocity of migration of a few typical lyophobe sols.

VELOCITY OF MIGRATION OF LYOPHOBE SOLS

Suspensoid	Average Diameter of Particles	Velocity cm./sec. for Unit Potential Gradient
Arsenic trisulphide	50 $m\mu$	22×10^{-5}
Quartz	1 $m\mu$	30×10^{-5}
Gold (colloidal)	<100 $m\mu$	40×10^{-5}
Platinum (colloidal)	<100 $m\mu$	30×10^{-5}
Silver (colloidal)	<100 $m\mu$	23.6×10^{-5}
Bismuth (colloidal)	<100 $m\mu$	11.0×10^{-5}
Lead (colloidal)	<100 $m\mu$	12.0×10^{-5}
Iron (colloidal)	<100 $m\mu$	19.0×10^{-5}
Ferric hydroxide (colloidal)	100 $m\mu$	$30\ 0\times10^{-5}$

It will be observed that not only are the velocities of migration nearly constant, but also that they are apparently independent of the size and nature of the particles. The presence of electrolytes, especially acids and bases, exercises a marked effect upon the electrical behavior of lyophobic colloids.

Many practical applications of cataphoresis have been developed lately, perhaps the most striking of which has been the actual plating out of gloves and other articles of rubber from a solution containing rubber latex.† Certain enamels are deposited on metal in a similar way. The charges on bacteria have been determined by observing the migration in a cataphoresis cell under a microscope, special precautions being taken to prevent any evolution of gas at the electrodes, which might cause a mechanical movement.

Electroendosmosis. It has been shown that colloid particles acquire an electrical charge opposite in sign to the dispersion medium

* J. chim. phys., **4**, 365 (1906).

† Sheppard, Trans. Am. Electrochem. Soc., **52**, 47 (1927).

and that they migrate to an electrode. The process may be reversed, and if the particles are held in a stationary position the liquid will move when an electrostatic field is applied. This phenomenon was first observed by Reuss and was subsequently explained by Perrin.*

If a porous partition is placed in the horizontal portion of a U-tube, and an electrode is inserted in each arm of the tube, it will be found, on filling the tube with a feebly conducting liquid and passing a current, that the liquid will commence to rise in one arm of the tube, and will continue to rise until a definite equilibrium is established. For a given difference of potential between the two electrodes, there will be a definite difference in the level of the liquid in the two arms of the tube. The majority of substances acquire a negative electric charge when immersed in water. The water, under these conditions, becomes positively charged and will, in consequence, migrate toward the cathode. On the other hand, certain substances acquire a positive charge on immersion in water, and in these cases the direction of migration will obviously be reversed.

It has been found that acids cause negative diaphragms to become less negative, and positive diaphragms to become more positive. The action of alkalies is, as we should expect, the reverse of that of acids. There is an interesting connection between the valence of the ions resulting from the dissociation of dissolved salts, and the difference of potential existing between the liquid and the diaphragm. When the diaphragm is positively charged, the difference of potential is found to be conditioned by the valence of the anion, and when the diaphragm is negatively charged, the difference of potential is determined by the valence of the cation.

The direction of electroendosmosis indicates the sign of the charge on the liquid. The experiments have been extended to organic liquids as well as to aqueous systems.† The drying of peat and other material by the application of an electrical field has been suggested, but there is a large loss of electrical energy if there are electrolytes present which conduct the current.

Precipitation of Colloids by Electrolytes. One of the most important and interesting divisions of the chemistry of colloids is that which treats of the precipitation of lyophobe and lyophile sols by electrolytes. Colloidal solutions are more or less unstable systems, irrespective of the methods employed in their preparation, and the addition of a small amount of an electrolyte is frequently found to be sufficient to cause the sol immediately to become opalescent, and

* J. chim. phys., **2**, 601 (1904).

† Mathews and Strickler, J. Am. Chem. Soc., **44**, 1647 (1922).

ultimately to precipitate, leaving the dispersion medium perfectly clear and free from the disperse phase.

The precipitation of lyophobe sols has been carefully investigated by Freundlich.* He found, that an amount of electrolyte which is incapable of bringing about an instantaneous precipitation, may become effective after an interval of time. He has also shown, that the total quantity of electrolyte required to precipitate a lyophobe sol completely, depends upon whether the electrolyte is added all at one time, or in successive portions.

In order to compare the precipitating action of various electrolytes, Freundlich proposed the following procedure, which diminishes the possibility of irregularities due to the time factor: — To 20 cc. of a solution of a lyophobe sol, 2 cc. of the solution of the electrolyte are added, the resulting solution being shaken vigorously; the mixture is then set aside for two hours, after which a small portion is filtered off, and the filtrate is examined for the colloid. In the following table, some of the results obtained by Freundlich with colloidal solutions of ferric hydroxide are given. The data represent the minimum concentration for each electrolyte which produced precipitation in two hours.

PRECIPITATING ACTION OF ELECTROLYTES ON FERRIC HYDROXIDE HYDROSOL

(16 milli-mols $Fe(OH)_3$ per liter)

Electrolyte	Concentration (milli-mols per liter)	Electrolyte	Concentration (milli-mols per liter)
$NaCl$	9.25	HCl	400 (approx.)
KCl	9.03	$Ba(OH)_2$	0.42
$BaCl_2$	9.64	K_2SO_4	0.204
KNO_3	11.9	$MgSO_4$	0.217
KBr	12.5	$K_2Cr_2O_7$	0.194
$Ba(NO_3)_2$	14.0	H_2SO_4	0.5 (approx.)
KI	16.2		

It will be seen that very small amounts of the electrolytes are required to precipitate the colloid, and further, that the precipitating power of an electrolyte is dependent upon the charge of the negative ion. The greater the charge, the smaller is the quantity of electrolyte required to produce precipitation.

The significance of the relation between ionic charge and precipitating power was first pointed out by Schulze, and later verified by

* Z. physik. Chem., **44**, 131 (1903).

Hardy. The rule of precipitation by electrolytes may be stated as follows: — *The precipitation of a colloid is effected by that ion of an added electrolyte which has an electric charge opposite in sign to that of the colloidal particles.*

It has already been pointed out that colloidal particles of arsenious sulphide are negatively charged; hence, according to the above rule, the positive ions of the added electrolyte will condition the precipitation of the lyophobe sol. The experiments of Freundlich confirm this prediction, as is shown by the following table:

PRECIPITATING ACTION OF ELECTROLYTES ON ARSENIOUS SULPHIDE HYDROSOL

(7.54 milli-mols As_2S_3 per liter)

Electrolyte	Concentration (milli-mols per liter)	Electrolyte	Concentration (milli-mols per liter)
KCl	49 5	$CaCl_2$	0.649
KNO_3	50.0	$SrCl_2$	0.635
$KC_2H_3O_2$	110.0	$BaCl_2$	0.691
NaCl	51.0	$Ba(NO_3)_2$	0.687
LiCl	58.4	$ZnCl_2$	0.685
$MgCl_2$	0.717	$AlCl_3$	0.093
$MgSO_4$	0.810	$Al(NO_3)_3$	0.095

It is evident that the trivalent ions are much more effective in precipitating colloids of opposite sign than are divalent ions and that the divalent ions are more effective than the univalent ions. There is no simple quantitative relation between the valence of the ion and the precipitating concentration because several other factors are involved also, such as the protective action of ions having the same sign as the colloid particles.

The action of electrolytes on lyophilic colloid sols is less sharply defined than their action on lyophobic colloids. Large concentrations of alkali salts are necessary to precipitate albumins, but small amounts of the heavy metals give precipitation on account of chemical reactions.

Dialysis. The marked difference between the rate of diffusion of crystalloids and colloids renders their separation comparatively easy. If a solution containing both crystalloids and colloids is separated from pure water by a colloidal membrane, such as parchment, the crystalloids will pass through the membrane and the colloids will be left behind. This process was termed *dialysis* by Graham, and the appa-

ratus employed to effect such a separation was called a *dialyzer.* When a solution of sodium silicate is added to an excess of hydrochloric acid and placed in a dialyzer, the resulting sodium chloride and the hydrochloric acid diffuse away, leaving colloidal silicic acid.

Various natural and artificial membranes may be used for dialysis; sacks of thin collodion are very satisfactory. These membranes contain small pores which provide continuous channels for the solution, through which dissolved molecules and ions can diffuse, but through which the large colloid particles cannot diffuse. Dialysis may be regarded as a process of fractional diffusion; it is not to be confused with osmosis in which nothing but solvent can pass through the semi-permeable membrane. The rate of dialysis depends on many factors — the size of the pores, the temperature, the electrical charges and the relative concentration of solution on the two sides of the membrane. In practical work fresh water is passed around the dialyzing sack to expedite the separation. Many colloids are prepared under conditions where an excess of ions is present and they are rendered more stable by dialysis. It is possible, however, to remove too many ions and cause coagulation. Sometimes the ions are removed by the passage of a current of electricity and the process is called electrodialysis.

Isoelectric Point. It has been shown that one factor in the stability of colloids is the electrical charge on the particles which tends to keep them separate. This charge is usually due to adsorbed ions and if these are removed by dialysis, the colloid particles are precipitated. On the other hand, if the solution surrounding the colloid particles contains too many ions, the charge on the particles will be neutralized by the ions of opposite charge and precipitation will occur. At the neutral point, where the particle and the solution have the same charge, the colloid has its minimum stability and this condition is defined as the *isoelectric point.* It is important in both lyophile and lyophobe colloids. Lyophile colloids such as albumin and gelatine are particularly responsive to a change in hydrogen ion concentration and in an acid solution they are charged positively on account of a chemical reaction and subsequent dissociation. In an alkaline solution they acquire a negative charge in the same way.

Protective Colloids. The precipitating action of electrolytes on lyophobic sols may be inhibited by adding to the solution of a lyophobic sol, a lyophilic colloid. The protective action of a lyophilic colloid is not due, as might be supposed, to the increased viscosity of the medium and the resultant resistance to sedimentation, since amounts of a protecting colloid, too minute to produce any appreciable increase in the viscosity of the medium, can prevent precipitation.

Thus, Bechhold* has shown that, while a mixture of 1 cc. of a suspension of mastic and 1 cc. of a 0.1 molar solution of $MgSO_4$, diluted to 3 cc. with water, is completely precipitated in 15 minutes, no precipitation will occur within 24 hours if 2 drops of a 1 per cent solution of gelatine be added before diluting to 3 cc. Gum arabic and ox-blood serum exert a similar protective action when added to a suspension of mastic.

The protective power of lyophilic colloids differs widely, and Zsigmondy† has attempted to make this the basis of a method of classification of colloidal substances. A red colloidal gold sol becomes blue on the addition of a small amount of sodium chloride, owing to the increase in the size of the colloidal particles. Various colloidal substances when added to a red colored gold sol protect the colloidal particles from precipitation by a solution of sodium chloride, no change in color following the addition of the electrolyte. A definite amount of each colloidal substance is required to prevent the change, from red to blue, in the color of the gold sol. In employing this color change as a means of differentiating colloidal substances, Zsigmondy introduced the so-called "gold number." This may be defined as the weight in milligrams of a colloidal substance which is just insufficient to prevent the change from red to blue in 10 cc. of a gold sol, after the addition of 1 cc. of a 10 per cent solution of sodium chloride. The following table gives the gold numbers of a few colloids.

GOLD NUMBERS OF COLLOIDS

Colloid	Gold Number
Gelatine	0.005–0.01‡
Casein (in ammonia)	0.01
Egg-albumin	0.15–0.25
Gum arabic	0.15–0.25; 0.5–4
Dextrin	6–12; 10–20
Starch, wheat	4–6 (about)
Starch, potato	25 (about)
Sodium stearate	10 (at 60°); 0.01 (at 100°)
Sodium oleate	0.4–1
Cane sugar	8
Urea	8

‡ Elliott and Sheppard, J. Ind. Eng. Chem., **13**, 699 (1921).

* Z. physik. Chem., **48**, 408 (1904).

† Z. anal. Chem., **40**, 697 (1901).

The gold number has proved useful in differentiating the various kinds of albumin, as is shown in the following table:

GOLD NUMBERS OF ALBUMINS

Albumin	Gold Number
Egg white (fresh).....	0 08
Globulin.....	0 02–0.05
Ovomucoid.....	0.04–0.08
Albumin (Merck).....	0.1–0.3
Albumin (cryst.).....	2–8
Albumin (alkaline).....	0.006–0.04

The addition of alkali to any one of the first five albumins of the above table reduces the gold number to that of alkaline albumin. Sulphide sols may be protected as well as metallic sols, and furthermore, the ability to exert protective action is not confined to organic colloids alone. It is in fact very important in preserving the character of sedimentary rocks and cements.

The gold number is useful also in diagnosing certain diseases, the spinal fluid from an afflicted person giving a gold number markedly different from that given by the spinal fluid from a healthy person.

In general, it may be said that, when a lyophobic sol is mixed with a lyophilic sol in the proper proportions, the lyophobic sol acquires most of the characteristic properties of the protecting colloid. The masking of the properties of a lyophobic sol by a protecting colloid is probably to be ascribed to the formation of a thin film of adsorbed lyophilic colloid over the lyophobic colloid.

Mutual Precipitation. A further deduction from the electrical theory of precipitation is, that when two oppositely charged colloids are mixed, they should precipitate each other, and the resulting precipitate should contain both colloids. Experiments carried out by Biltz* have confirmed these predictions. He showed that when a solution of a positively charged colloid is added to a solution of a negatively charged colloid, precipitation occurs, unless the quantity of the added colloid is either relatively very large, or very small. Just as the amount of precipitation caused by the addition of an electrolyte to a sol is conditioned by the rate at which the electrolyte is added, so also the precipitation of one colloid by another is dependent upon the manner in which the two sols are mixed. The extent to which one sol is precipitated by another sol of opposite sign is largely determined by

* Ber., **37**, 1095 (1904).

the amount of the one that is added to a definite amount of the other. This is clearly shown by the following table, which gives the results obtained by Biltz, on adding ferric hydroxide sol to 2 cc. of an antimony trisulphide sol containing 2.8 mg. per cc.

PRECIPITATION OF COLLOIDAL ANTIMONY TRISULPHIDE BY COLLOIDAL FERRIC HYDROXIDE

Fe_2O_3(mg.)	Immediate Result	Result After One Hour
0.8	Cloudy	Almost homogeneous
3.2	Small flakes	Unchanged
4.8	Flakes	Yellow liquid
6.4	Complete precipitation	Complete precipitation
8.0	Slow precipitation	Complete precipitation
12.8	Cloudy	Slight precipitation
20.8	Cloudy	Homogeneous

It will be seen that the addition of a small amount of ferric hydroxide produces hardly any precipitation. With the addition of larger amounts of ferric hydroxide, the amount of precipitation increases, until finally, complete precipitation is attained. The addition of larger quantities of ferric hydroxide produces either little, or no, precipitation. It has been found, that at the concentration which just produces complete precipitation, the electrical charges of the two sols are equivalent.

Preparation of Colloids. After studying the properties of colloids it is easy to understand the methods by which they can be prepared, but the details of the methods* are beyond the scope of this book.

The various methods for the production of colloidal systems may conveniently be divided into two classes, as follows: (1) Methods in which relatively coarse material is subdivided into fine particles, and (2) methods in which the minute particles, molecules, or atoms of a substance are gathered together to form particles of colloidal dimensions. Methods belonging to the first class are termed "dispersion methods"; those belonging to the second class are known as "condensation methods." In dispersion methods the relative surfaces of the systems are increased, whereas in condensation methods the relative surfaces are decreased. In general, it may be said that condensation processes are more common than dispersion processes.

It is not always possible, at first sight, to determine whether a given process involves dispersion, or condensation. For example, when a colloidal sol is prepared by forming an electric arc between two metal

* The best references in this field are Svedberg's "Colloid Chemistry" and "The Formation of Colloids."

wires immersed in a liquid, the metal is at first vaporized by the arc, and subsequently condenses to form particles of larger dimensions.

Dispersion Methods. The so-called "colloid mill"* is one of the most important and promising devices for the production of colloidal solutions by the dispersion method. The substance to be dispersed is suspended in the dispersion medium in the form of coarse particles. The suspension is then introduced into the colloid mill, where an exceedingly high velocity is imparted to one portion of the suspension, while the other portion either remains at rest, or is caused to rotate at high speed in a direction opposite to that of the first portion. This is accomplished by passing the liquid through a channel in a shaft on which two metal discs rotate at high speed in opposite directions. As the suspension flows out in a thin layer between the two oppositely rotating discs, the suspended particles are subjected to an intense shearing stress under which they rapidly disintegrate. In order to produce a high degree of dispersion, a peripheral speed of 30 m. per sec. has been found necessary. All previous attempts to produce colloidal systems by purely mechanical means have failed, but the success of the colloid mill is proved by its extensive application in the industrial production of colloids.

Condensation Methods. In 1897, Bredig† discovered, while studying the action of the electric current on different liquids, that if an arc is established between two metallic wires immersed in a liquid, minute particles of metal are torn off from the negative terminal and remain suspended in the liquid indefinitely. In order to prepare a colloidal solution by the method of electrical dispersion, Bredig recommends that a direct current arc be established between wires of the metal of which a colloidal solution is desired, the ends of the wires being submerged in water in a well-cooled vessel, as shown in Fig. 80. The current employed ranges in strength from 5 to 10 amperes, and the voltage lies between 30 and 110 volts. A rheostat and an ammeter are included in the circuit.

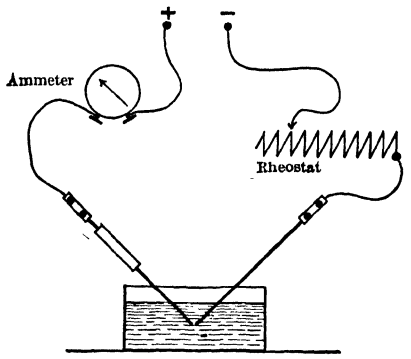


FIG. 80

* Kenney, Chem. & Met. Eng., **27**, 1080 (1922); Travis, "Mechanochemistry and the Colloid Mill."

† Z. Elektrochem., **4**, 514 (1897); Z. physik. Chem., **31**, 258 (1899).

The wires are brought in contact for an instant in order to establish the arc, after which they are separated about 2 mm. Clouds of colloidal metal are projected out into the water from the negative wire, portions of the metal torn off being distributed through the water as a coarse suspension. The size of the particles disrupted from the negative terminal is dependent upon the strength of the current, a current of 10 amperes producing a greater proportion of colloidal metal than a current of 5 amperes. The addition of a trace of potassium hydroxide to the water has been found to stabilize the dispersed metal. When gold wires are used, deep red colloidal solutions are obtained, which, after standing for several weeks, acquire a bluish-violet color. With extra precautions, the red colloidal gold solutions may be preserved for many years. Bredig's solutions contained about 14 mg. of gold in 100 cc. In this manner, Bredig prepared colloidal solutions of platinum, palladium, iridium, and silver.

Svedberg and his co-workers,* as the result of a closer study of the direct current arc, have shown that the production of metallic vapor can be greatly increased by protecting the electrodes from the cooling effect of the surrounding liquid. The colloidal particles in sols obtained with the protected arc have an average diameter of 5 $m\mu$, while those produced with the unprotected arc are approximately 25 $m\mu$ in diameter. Spectrograms of the free arc reveal that relatively little of the dispersion medium is decomposed in the case of the protected arc.

By means of an oscillatory arc, Svedberg and his co-workers have succeeded in preparing sols of all available metals, including those of the alkalies. In the case of the latter, ether, free from water and oxygen, is employed as the dispersion medium.

It is possible under suitable conditions to condense vapor directly into small particles of colloid dimensions. Roginsky and Scholnikoff,† for example, obtained a colloidal solution of sodium in benzene by collecting sodium vapor and benzene vapor on a surface chilled by contact with liquid air.

Material in solution may sometimes be thrown out in the colloidal state by mixing it with a second solvent in which the material is less soluble. For example, sulphur dissolved in alcohol is obtained as a white milky colloid solution when poured into an excess of water.

It will be noted that in these methods no appreciable quantity of electrolyte has been present. In fact, colloids can be produced by almost any chemical reaction which would normally give a precipitate, provided that the concentration of electrolytes is kept sufficiently low.

* Svedberg, " Formation of Colloids," p. 25.

† Kolloid Z., **43**, 67 (1927).

A few special reactions which are favorable in this respect are as follows:

$$As_2O_3 + 3\ H_2S = As_2S_3 + 3\ H_2O,$$
$$2\ H_2S + SO_2 = 3\ S + 2\ H_2O,$$
$$Ni(CO)_4 = Ni + 4\ CO.$$

In the first reaction, if arsenious chloride is used in place of the arsenious oxide, hydrochloric acid will be produced in the reaction instead of water, and the arsenious sulphide will be partially coagulated.

Even when electrolytes are produced, it is possible to obtain the precipitate in the colloidal state if the solutions are dilute. As already pointed out, the colloids may be rendered more stable by adding a protecting colloid such as gelatine, or by removing the electrolytes with a dialyzer.

Although most of the examples have been confined to colloid systems in which solids are suspended in liquids, it must be emphasized that it is possible to prepare colloid systems in which gases are dispersed in liquids (foams); solids in gases (fumes); liquids in gases (mists); and solids, liquids and gases dispersed in solids. The important case of liquids dispersed in liquids (emulsions) will be studied presently.

Lyophilic and Lyophobic Colloids. The relation between the lyophilic colloids in which there is an affinity between the dispersed phase and the dispersion medium, and the lyophobic colloids in which no such affinity exists is well illustrated in Fig. 81. The lyophilic colloid particles are hydrated with an atmosphere of the dispersion medium whereas the lyophobic colloids are not. Either the electrical double layer, or the hydrating atmosphere, or both together, are sufficient to keep the system in the colloidal state. The particles become coagulated and the system loses its colloidal properties only when both the electrical double layer and the hydrating atmosphere are removed. Egg albumin may be taken as an example. Its particles can be dehydrated with alcohol and the charge can be neutralized, but only when *both* changes are effected can coagulation occur.

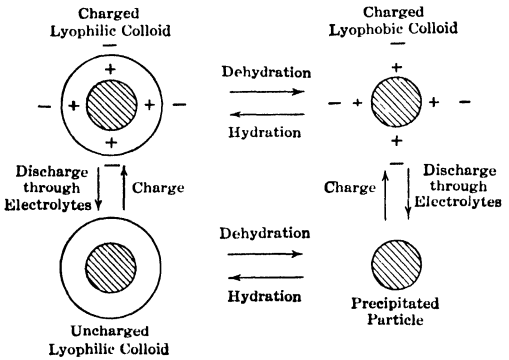


FIG. 81

Emulsions. A dispersion of minute drops of one liquid in another is known as an *emulsion*. If an emulsion contains relatively little of the disperse phase, its properties resemble those of the lyophobe sols. That is, the disperse phase exhibits the Brownian movement, is precipitated by electrolytes, and can even be separated from the dispersion medium by the process of ultrafiltration.

Two liquids which are mutually insoluble may be emulsified by prolonged mechanical agitation, but if the resulting emulsion contains much more than 1 per cent of the disperse phase, it is unstable, and the component liquids soon separate into two layers. For example, a small portion of benzene in a large volume of water may be emulsified by shaking, but on standing, the minute droplets of benzene soon coalesce and the liquids separate into two layers. The larger the proportion of benzene in the mixture, the more unstable the emulsion becomes.

While stable emulsions of two pure liquids cannot be prepared, they may readily be stabilized by the addition of a third substance known as an *emulsifying agent*, or *emulsifier*. Thus, if a small amount of sodium oleate is dissolved in water and this solution is vigorously shaken with benzene, a stable emulsion will result. Emulsions of kerosene in water, containing as high as 99 per cent of oil in a 1 per cent soap solution, have been prepared and studied by Pickering. The emulsion containing 99 per cent of kerosene was found to resemble a solid, and had the consistency of blanc mange. It frequently happens that a small amount of unsuspected impurity functions as an emulsifying agent.

Two main types of emulsion are recognized: (1) emulsions in which oil is dispersed in water, known as the *oil-water* type, and (2) emulsions in which water is dispersed in oil, known as the *water-oil* type. The word "oil" is here used to designate any liquid which is insoluble in water. Of these two types of emulsion, the first is by far the more common.

Although the alkali soaps are excellent emulsifying agents for emulsions of the first type, it has been found that they are not satisfactory for emulsions of the second type. On the other hand, though the soaps of the heavy metals are not good emulsifying agents for emulsions of the first type, they are found to be most effective for those of the second type. Gum arabic, gelatine, agar-agar, albumin, and all the so-called "solvated colloids" are also good emulsifying agents.

Although it is often difficult to decide from a superficial examination whether an emulsion is of the oil-water or water-oil type, the question may be definitely answered by placing a few drops of the emulsion under the microscope and stirring in successively a little of

one phase, and then a little of the other. The external phase will readily mix with the emulsion; the internal phase will not.

The preparation of stable emulsions is of great practical importance in pharmacy, in cooking, and in many industrial operations. Mechanical homogenizers are arranged to mix intimately two immiscible liquids by producing very fine droplets of one in the other. The cleansing action of ordinary soap depends in large measure on its ability to produce an emulsion of oil in water. The large surface of the emulsion droplets is effective in removing dirt and grease. One of the most important processes now used in mining operations for concentrating the valuable part of an ore is that of ore flotation. It is a process by which an oil emulsion and foam are produced and the mineral particles rise to the surface where the material is concentrated.

The reverse process of breaking up emulsions, known as "de-emulsification," is also of considerable practical importance. For example, petroleum frequently contains large amounts of emulsified water which it is very desirable to remove. Several methods are available for de-emulsification; among these may be mentioned the Cottrell process, employing a high-voltage precipitator, and methods based upon filtration, freezing out and centrifugal separation. The last method is extensively used in dairies for separating cream.

Theories of Emulsification. Numerous theories have been advanced in explanation of the phenomena of emulsification. Thus, it was believed by Plateau and Quincke that the important function of the emulsifying agent is its power to lower the interfacial tension between the two liquids forming the emulsion. The alkali soaps which have been mentioned as among the best known emulsifying agents are known to produce marked lowering in the surface tension of water. For example, in an emulsion of benzene and water, the interfacial tension is approximately 35 dynes per cm., but when enough sodium oleate is dissolved in the water to make the solution 0.01 molal, the interfacial tension is reduced to about 2 dynes per cm.

According to another theory, emulsifying power is ascribed to the tendency of the emulsifying agent to form hydrates and, thus, bind to itself the molecules of the aqueous phase.

Bancroft* holds that the type of emulsion is determined by the phase which is the best solvent for the emulsifying agent. He maintains that, "If the adsorption of the emulsifying agent lowers the surface tension on the water side of the interface more than it does on the oil side, the interface will tend to curve so as to be concave on the water side, and we shall have a tendency to emulsify oil in water. If the

* Bancroft, "Applied Colloid Chemistry," p. 261.

adsorption of the emulsifying agent lowers the surface tension on the oil side of the interface more than it does on the water side, the interface will tend to curve so as to be concave on the water side, and we shall have a tendency to emulsify water in oil. The simplest way, then, to emulsify oil in water is to add a water-soluble colloid which is adsorbed strongly at the interface, and the simplest way to emulsify water in oil is to add an oil-soluble colloid which is adsorbed strongly in the interface."

It has been shown by Bhatnagar* that all emulsifying agents having an excess of negative ions adsorbed on them, and wetted by water, yield oil-in-water emulsions, while emulsifying agents having an excess of adsorbed positive ions, and wetted by oil, yield water-in-oil emulsions.

According to another theory, the most effective emulsifying agents are those whose molecules consist of long chains of carbon atoms with a strong polar group, such as the carboxyl group, at one end. The nonpolar end of the molecule is assumed to direct itself towards the oily liquid, while the polar end tends to enter the aqueous phase. If the nonpolar ends of the molecules can pack together more closely than the polar ends, the interfacial film will be bent towards the oil, and an emulsion of oil in water will result. This is commonly known as the oriented wedge theory of emulsification. The theory has been developed by Hildebrand,† who has endeavored to show how it may be applied to the behavior of all emulsifying agents for which the necessary data are available, but it is not thoroughly established.‡

Gels. When the conditions within a solution are so modified as to depress the solubility of the solute below a certain definite value precipitation may occur, and the resulting precipitate may be crystalline or amorphous in character, depending on the time taken to precipitate and on other factors. Von Weimarn has shown that the degree of supersaturation at the time of formation and the viscosity of the medium account, qualitatively at least, for the observed phenomena. For example, when barium sulphate is precipitated from very dilute solutions it is possible to obtain small crystals. When the solutions are more concentrated the state of supersaturation after mixing is greater and the crystals become less pronounced. When the solutions contain about one equivalent per liter an immediate precipitate is formed which is apparently amorphous. With still more concentrated solutions (3 to 7 equivalents per liter of barium sulphocyanate and manganese sulphate) a clear jelly is produced.

* J. Chem. Soc., **119**, 61, 1760 (1921).

† Finkle, Draper and Hildebrand, J. Am. Chem. Soc., **45**, 2780 (1923).

‡ Stamm and Kraemer, J. Phys. Chem., **30**, 992 (1926).

It is obvious then that we should not speak of crystalloidal and colloidal matter but rather of the crystalloidal and colloidal states. In fact, it is now recognized that it is simply a matter of overcoming experimental difficulties before it will be possible to obtain all forms of matter in the colloidal state.

When the precipitate retains an appreciable quantity of the liquid in which it was dissolved in the form of a semi-rigid mass it is termed a "gelatinous precipitate," and if all the liquid is initially retained a jelly or *gel* is produced.

The production of gels by the cooling of a sol is one of the simplest and most familiar methods. As an example of this method, we may cite the formation of a typical gel by cooling to room temperature a 2 per cent gelatine sol in hot water. The resulting gel will be found to be both stiff and transparent. It seems probable that when such a sol cools, the molecular aggregates unite to form long filaments which interlace and give rise to a structure resembling a heap of brushwood. Such a structure would account for the entangling of a large volume of water in the capillary spaces. It is highly probable, however, in gels with well developed structure, that the aggregates of the gel-forming substance are hydrated by the adsorption of water, with a consequent thickening of the filaments. In such a gel, the water which is not actually adsorbed is probably held by capillary attraction.

Gels may be produced also by metathesis, as when an acid is mixed with sodium silicate in suitable concentrations. In concentrated solutions the resulting silicic acid forms a stiff, transparent gel immediately, but in very dilute solutions the completion of the gel may be delayed for fully a month.

A gel may be formed by changing the solvent as, for example, when chloroform is added to a nitrocellulose sol in amyl acetate. Coagulation occurs and a transparent, viscous gel is obtained. It is of interest to note that when the gel is pressed between the fingers, it is possible to remove nearly all the liquid, leaving a mass of cotton-like fiber in the hand. Apparently the greater part of the liquid is retained by the capillary action of the fibers.

By carefully regulating the concentration of ions, it is possible in some cases to coagulate a hydrated sol to give a gel.*

In a preceding section of this chapter it was pointed out that in an emulsion the emulsifying agent is concentrated at the interface between the disperse and continuous phases. It can be shown that if the disperse phase is in the form of spherical close-packed drops, like oranges in a box, their combined volume will represent about 74 per

* Weiser, J. Phys. Chem., **26**, 430 (1922).

cent of the total volume. Obviously when the aggregate volume of the disperse phase exceeds that corresponding to close packing, a flattening of the drops must occur and, in consequence, a honeycomb structure will gradually develop. Thus, a 75 per cent emulsion of kerosene in water, to which 0.4 per cent of gelatine has been added as an emulsifying agent, forms a gel of such rigidity that scarcely any evidence of flow is observed when a tube containing the emulsion is inverted.

Properties of Gels. On standing, gels frequently undergo an appreciable shrinkage in volume with a simultaneous extrusion of liquid. This phenomenon is called *syneresis*. When placed in a dry atmosphere gels quickly dry out, and when placed in water they take up water, rapidly at first, and then more slowly. The rate depends on the difference between the weight of water which the gel holds and the maximum amount which it can hold. When placed in a salt solution, the salt distributes itself between the solvent and the gel, and the rate of distribution varies greatly with the different ions. The mechanical work done by the expansion of a gel during imbibition of water is very large and constitutes a large fraction of the observed heat. This fact is important because the swelling of gels is the mechanism of muscular action.

The behavior of gels on freezing depends largely on the amount of unadsorbed water and this relation is important in explaining the winter hardiness of certain types of seeds.

When a moderately concentrated solution of gelatine is cooled, it sets to a stiff jelly or gel, which is again readily converted into a sol on warming. The change is reversible in gelatine, but in albumin and certain other lyophilic colloids a chemical change accompanies the heating, and irreversible coagulation occurs, as in the boiling of an egg.

In studying the phenomenon of gelation, either the temperature or the time of gelation may be determined. Both vary with the concentration, a 5 per cent solution of gelatine undergoing gelation at 18° and solation at 26° and a 15 per cent solution undergoing gelation at 25° and solation at 29°. The behavior of a complex substance like gelatine is not reproducible but depends largely on the source of material, its purity and previous history.

A surprisingly large number of common things of importance are gels, including soap, wood, resins, "Bakelite," certain animal tissues and rubber.

Lyotropic Series. Salts have a marked effect on the temperature of the gel-sol transformation, some tending to raise the temperature of gelation and others to lower it. The effect is not to be explained on

the basis of ionic charge and, in fact, univalent ions give widely different results. Hofmeister arranged the negative ions of sodium salts in the following order, the first having the greatest influence in lowering the temperature of gelation and the last one the least influence.

$$SCN^- > I^- > Br^- > NO_3^- > ClO_3^- > Cl^- > C_2H_3O_2^- > SO_4^{--}. \quad (6)$$

Several attempts have been made to explain why these ions have this specific action, but none has seemed entirely satisfactory. Although some investigators have doubted the significance of such a series, it finds real application in several different fields and must be accepted as an empirical fact. The same sequence of ions is maintained not only in the gelation temperature of agar-agar and other similar substances, but also in their rate of swelling.

Surface Concentration. The rest of the chapter will be devoted to the study of surface phenomena. The mathematical relation between surface concentration and surface tension was first deduced by J. Willard Gibbs* in 1876. The following simplified derivation of this important relation is due to Ostwald. Let s be the surface of a solution whose surface tension is γ, and whose surface layer contains an excess of 1 mol of the solute. If a very small portion of the solute enters the surface layer from the solution, thereby causing a diminution $d\gamma$, in the surface tension, the corresponding change in energy will be $s\,d\gamma$. But this amount of energy which is set free must be equivalent to the osmotic work done in effecting the removal of the same weight of solute from the solution. Let v be the volume of solution containing 1 mol of solute, and let dp be the difference in the osmotic pressures of the solution before and after removal of an infinitesimal quantity of solute: the osmotic work will be $-v\,dp$. Since the gain in surface energy and the osmotic work are equal, we have

$$s\,d\gamma = -v\,dp. \quad (7)$$

The solutions being dilute, we may assume that the gas laws hold, and since $v = RT/p$, we may write,

$$s\,d\gamma = -\frac{RT}{p}\,dp, \quad (8)$$

or

$$\frac{d\gamma}{dp} = -\frac{RT}{sp}. \quad (9)$$

Since pressure is directly proportional to concentration c, the preceding equation becomes

$$\frac{d\gamma}{dc} = -\frac{RT}{sc}. \quad (10)$$

* Trans. Conn. Acad., Vol. III, 439 (1876).

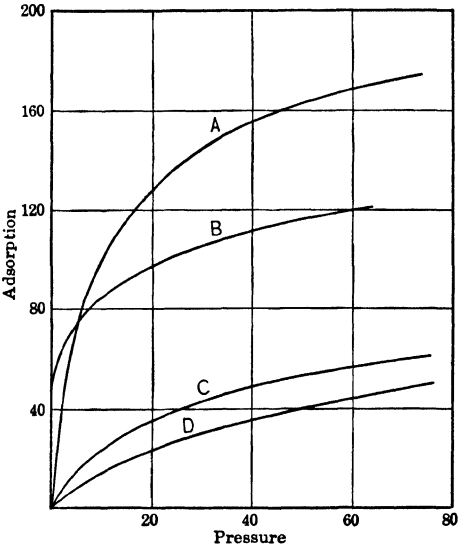
Writing u for $1/s$ we have the equation of Gibbs, as follows:

$$u = -\frac{c}{RT}\frac{d\gamma}{dc}, \tag{11}$$

where u is the excess of solute in the surface layer per sq. cm. of surface.

From this equation it is evident, that if the surface tension, γ, increases with the concentration, then u is negative, and the surface concentration is less than the concentration of the bulk of the solution. On the other hand, if γ decreases as the concentration increases, u is positive, and the surface concentration is greater than the concentration of the bulk of the solution. Finally, if the surface tension is independent of the concentration, then the concentration of the solute in both the surface layer and the bulk of the solution will be the same.

It may be concluded further that the surface tension of a liquid can be lowered to a considerable extent by the addition of a solute because the solute will then concentrate in the surface and register a large effect, but the surface tension can never be increased very much by the addition of a solute because, in this case, it is held chiefly by the bulk of the solution where it can exert no influence on surface phenomena. This deduction is well confirmed by experiment. Soaps and other material are known to reduce the surface tension of water by more than half, but no substance has yet been discovered which will raise the surface tension more than a few per cent.



A. Ammonia on charcoal at 0° C.
B. Ammonia on meerschaum at 0° C.
C. Carbon dioxide on charcoal at 0° C.
D. Argon on charcoal at −78.3° C.

FIG. 82

Experimental tests of this equation are difficult because the real surface layer contains such a small amount of dissolved material, but it is believed that the equation is essentially correct. In one of the best tests yet available, froth and foam were swept out from a soap solution and the concentration in this

froth was found to be greater than that in the bulk of the solution left behind.

Adsorption. The tendency exhibited by all solids to condense upon their surfaces a layer of any gas or liquid with which they are in contact is termed *adsorption.* The amount of adsorption is conditioned by the extent of the surface exposed, by the pressure or concentration, by the temperature and also by the specific nature of the adsorbent and that of the adsorbed substance. Very little is known of the surface tension of solids, and accordingly there has been no opportunity to apply the equation of Gibbs.

The retention of gases by charcoal and the removal of dyes, such as methylene-blue with charcoal, are examples of adsorption.

At a given temperature and pressure a given sample of charcoal is found to adsorb a definite quantity of gas. If the pressure is increased, it will adsorb more; if it is decreased, it will adsorb less; but on restoring the pressure to its initial value the amount of gas adsorbed is found to be the same as that originally taken up. In other words, an adsorption equilibrium is reached. If the pressures are plotted against the quantities of gas adsorbed, curves similar to those of Fig. 82 are obtained. Such curves are known as *adsorption isotherms* since they represent the variation of adsorption with pressure at constant temperature.

Adsorption from solution is illustrated by the data of the following tables for acetic acid and benzoic acid adsorbed by charcoal. x denotes the weight of adsorbed material and m the weight of adsorbing material. x/m then is the weight adsorbed per gram of charcoal. The concentration, c, which is in equilibrium with the adsorbed material on the charcoal, is given in the first column.

Adsorption of Acetic Acid in Water by Charcoal at 25° C.		Adsorption of Benzoic Acid in Benzene by Charcoal at 25° C.	
c	x/m	c	x/m
0 018	0.467	0.0062	0.437
0.031	0.624	0.025	0.78
0.0616	0.801	0.053	1.04
0.126	1.11	0.118	1.44
0.268	1.55		
0.471	2.04		
0.882	2.48		
2.79	3 76		

The data are plotted in Fig. 83; it is seen that the curves are of the same form as those describing gaseous adsorption.

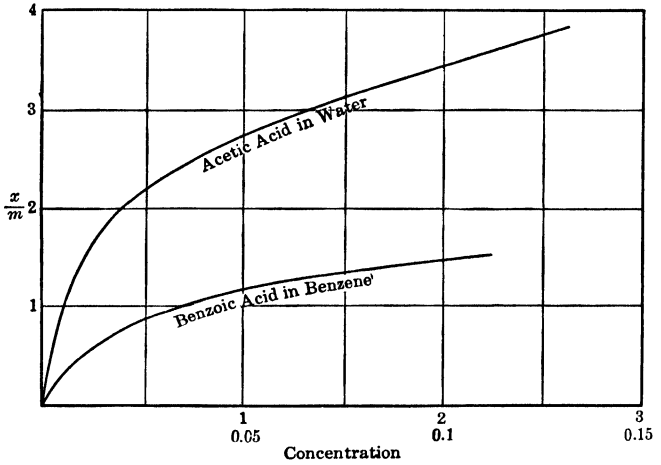


FIG. 83

Adsorption data of this type may often be represented by the empirical equation of Freundlich,

$$\left(\frac{x}{m}\right)^n = kc, \tag{12}$$

where k and n are constants to be determined by experiment for each

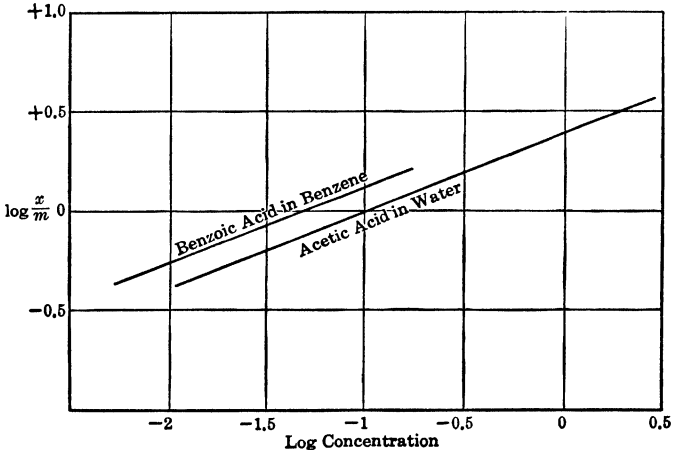


FIG. 84

temperature. The fact that this equation represents the data fairly well may be seen from Fig. 84 where log x/m is plotted against log c.

By taking logarithms of both sides of the Freundlich equation it is evident that a straight line should result having the slope $1/n$, and the intercept $1/n \log k$.

Similar results can be obtained with gases in which the pressure p is substituted for the concentration c.

No very definite generalization concerning the behavior of adsorbents can be formulated. Charcoal, whether of vegetable or animal origin, is probably the most powerful adsorbent known. Silica gel, the dehydrated gel of silicic acid, is another effective adsorbent which finds extensive scientific and industrial applications.

Since adsorption diminishes as the temperature is raised, it follows that in order to obtain a high degree of adsorption a low temperature must be maintained. Thus, in removing the last traces of vapor in the production of high vacua, the apparatus to be exhausted is connected with a vessel cooled in liquid air and containing a good grade of adsorbent charcoal.

Adsorption in solution is largely dependent upon the surface tension of the solvent. In solutions of the same substance in different solvents, the greatest adsorption occurs in that solution whose solvent possesses the highest surface tension.

The order of efficiency of adsorption is not only generally independent of the nature of the solvent, but also of the nature of the adsorbed substance.

Exchange Adsorption. The phenomena attending the adsorption of suitable electrolytes by difficultly soluble salts, such as kaolin, are of special interest. If, for example, a solution of methylene-blue chloride, which is strongly ionized in aqueous solution, is shaken up with kaolin, the adsorption will be found to differ in several respects from the adsorption of a non-ionized solute by an insoluble adsorbent, such as charcoal. Thus, only the cation of the dye is adsorbed, while the chloride ion remains behind in the solution with its concentration practically unaltered. Since the electrical neutrality of the solution must be preserved through the presence of an equivalent number of cations and anions, the adsorption of the cations of methylene-blue must be offset by the removal from the adsorbent of an equivalent number of positively charged ions. In the example under consideration, electrical neutrality is found to be preserved by the removal of positively charged calcium ions from the kaolin. This type of adsorption is known as *exchange adsorption*. It should be observed that this type of adsorption is polar in character, as distinguished from the adsorption of non-electrolytes, which is nonpolar. Notwithstanding the differences between polar and nonpolar adsorption, the two proc-

esses have been found, at low concentrations, to follow the exponential law expressed by the adsorption isotherm.

The behavior of artificial permutite affords an interesting example of exchange adsorption. This substance takes up calcium ions from solution and gives up an equivalent number of sodium ions; or under other conditions, a sodium permutite may give up nearly all of its sodium ions in exchange for silver ions. In the latter case, therefore, silver will have almost completely replaced sodium throughout the entire space lattice of the permutite.

These experiments would seem to indicate that siliceous adsorbents possess a more or less porous structure, and that even the silicate ions themselves may form an open framework through which the cations can freely circulate.

Adsorption undoubtedly plays an important rôle in both biological and physiological processes, the cell walls adsorbing dissolved substances in a manner quite analogous to the behavior of ordinary adsorbents. For example, it has been shown that the action of veratrine on the cardiac muscle of a certain variety of marine snail exhibits all the characteristics typical of an adsorption. The drug is taken up quickly and reversibly, it can be removed by prolonged treatment with water, and the process follows the simple exponential law expressed by the adsorption isotherm.

Theory of Adsorption. The Freundlich equation is useful as an empirical formula but a better equation has been developed by Langmuir.* Its derivation is based on the well established view that a solid has a crystal lattice and that its surface is like a checkerboard with atoms arranged in orderly fashion. Each atom at the surface has free valencies or unattached forces which are available for attaching one, and only one, molecule from the gas phase or from solution. There is a continuous flight of molecules from the external phase to the surface and in the opposite direction. The rate at which molecules are adsorbed depends on three factors: (1) the number s striking the surface (which can be calculated from the kinetic theory of gases); (2) the fraction m of incident molecules which adhere; and (3) the area $(1 - g)$ which is not covered by adsorbed molecules, g being the fraction covered. The rate of desorption is gr, where r is the rate of evaporation from a completely covered surface.

At equilibrium

$$gr = ms\,(1 - g) \tag{13}$$

$$g = \frac{ms}{r + ms}. \tag{14}$$

* J. Am. Chem. Soc., **38**, 2267 (1916); **40**, 1361 (1918).

Substituting l for the constant, m/r,

$$g = \frac{ls}{1 + ls}. \tag{15}$$

Using different constants, a and b, the weight of adsorbed material, y, per unit surface of adsorbing material is given by the formula

$$y = \frac{abp}{1 + ap}, \tag{16}$$

where p is the pressure of the gas. Concentrations c may be used instead of pressures and y may be considered proportional to the weight of adsorbed material per weight of adsorbing material.

This formula fits many experimental data very well. In fact, the agreement constitutes an argument in favor of the underlying assumption of an adsorbed layer one molecule deep. At very high pressures it does not apply so well in some cases, probably because under these conditions a new type of adsorption is occurring, namely, the liquefaction of the gas in capillary pores. Under these conditions the layer is of course many molecules deep and there is other evidence of condensation. Patrick found that, on silica gel, where the capillary type of adsorption prevails, the quantity of different gases adsorbed under similar conditions depends chiefly on the boiling-point. Taylor has been able from thermal measurements of adsorption to distinguish between (1) chemical adsorption by attachment to an atom at a surface, and (2) physical adsorption by condensation to a liquid. The evolution of heat in (1) may be several times that in (2).

It is significant that improved experiments tend more and more to support the Langmuir formula and its underlying hypotheses, when the adsorption is not too great. Measurements of the quantity of water adsorbed on glass surfaces seemed to indicate that the layer must be several molecules deep, but repetition of the work with fresh glass surfaces that had never been etched by contact with liquids showed that the adsorbed layer is probably one molecule thick.* In an important series of investigations in which adsorbed material was weighed with a small spiral spring of quartz, McBain† has shown that if the adsorbing surface is absolutely clean the Langmuir formula applies satisfactorily, whereas the Freundlich formula can be applied if the adsorbing surface contains impurities.

* Frazer, Patrick and Smith, J. Phys. Chem., **31**, 897 (1927).

† McBain and Britton, J. Am. Chem. Soc., **52**, 2198 (1930).

REFERENCES

Colloid Chemistry. Svedberg.
Colloids. Kruyt.
Treatise on Physical Chemistry, Chapter XX, Taylor (Kraemer).
An Introduction to the Physics and Chemistry of Colloids. Hatschek.
The Chemistry of the Colloid State. Ware.
Applied Colloid Chemistry. Bancroft.
An Introduction to Surface Chemistry. Rideal.
Colloid and Capillary Chemistry. Freundlich (translated by Hatfield).
Colloid Chemistry, Theoretical and Applied. Vols. I and II. Alexander.
Outlines of Biochemistry. Gortner.
Colloid Science Applied to Biology, Symposium Faraday Society. Trans. Faraday Soc., **26**, 667–864 (1930).
Colloid Symposium Monographs. Nos. I to VII.

PROBLEMS

1. Assuming that in a colloidal solution of silver each particle is a cube 50 $m\mu$ on an edge with a density of 10.5. (*a*) How many colloid particles can be produced from 0.1 g. of silver? (*b*) What is the total area of the silver particles?

2. A mercury sol is composed of globules having a diameter of 40 $m\mu$. What is the surface of the particles formed from 1 g. of mercury?

3. A sol containing 0.00139 g. Fe_2O_3 per cc. was diluted one part to 10,000. Ultramicroscopic count on the dilute sol gave an average of 2.87 particles per count in a field of view of 0.03 mm. diameter and 0.03 mm. depth. Assuming the density of the particle to be 5.2, and that the particles are cubes, what is the length on an edge of the particles?

4. The number of particles in a given volume of gold sol which had come to equilibrium in a gravitational field was found to be 386 at one level and 193 at a level 0.10 mm. higher. The temperature was 19° C. and the diameter of the particles was 66 $m\mu$. The specific gravity of gold is 19.3 and that of the sol may be assumed to be 1. What value of Avogadro's number is obtained from these data?

5. One cubic centimeter activated charcoal may have a surface area of 1000 square meters. Assuming, as a limiting case, complete surface coverage, how much ammonia, at standard conditions, could be adsorbed on the surface of 55 cc. activated charcoal? The diameter of the NH_3 molecule is 3×10^{-8} cm.

6. What values of the constants k and n of Freundlich's equation represent the adsorption of acetic acid on charcoal from a water solution, as given by the table on page 238?

7. The adsorption of N_2 on mica is as follows:

p	$\frac{x}{m}$
2.8	12
6.1	19
17.3	28.2
23.8	30.8

(p is given in dynes per sq. cm. and x/m as the cu. mm. of gas at 20° C. and 760 mm. adsorbed on 24.3 g. of mica, having a surface of 5750 sq. cm.) Determine the constants of Freundlich's equation and calculate the value of x/m when $p = 34$. (The experimental value is $x/m = 33$.)

8. Show that Langmuir's equation may be written in the form $\frac{p}{y} = \frac{1}{ab} + \frac{p}{b}$. $y = x/m$. The constants a and b may be determined from the data of the preceding problem by plotting $\frac{p}{y}$ against p. The straight line thus obtained has a slope $\frac{1}{b}$ and an intercept $\frac{1}{ab}$. What are the values of the constants and what is the calculated value of y when $p = 34$?

Ans. $a = 0.155$, $b = 39$, $y = 32.8$ when $p = 34$.

CHAPTER XI

THERMOCHEMISTRY

Thermal Units. Thermochemistry is concerned with the thermal changes which accompany chemical reactions.

Heat is a form of energy, and, as already shown, it may be resolved into two factors: an intensity factor, the temperature; and a capacity factor, the heat capacity. The product of these two factors, the thermal energy, may be measured in terms of any one of several units among which those defined below are most frequently employed.

The *small calorie* (cal.) is the quantity of heat required to raise the temperature of 1 gram of water from 15° to 16° C. The temperature interval is specified because the specific heat of water varies with the temperature. The *large* or *kilogram calorie* (Cal.) is the quantity of heat required to raise the temperature of 1000 grams of water from 15° to 16° C. The *Ostwald* or *average calorie* is the quantity of heat required to raise the temperature of 1 gram of water from 0° to 100° C. It is approximately equal to 100 cal., or to 0.1 Cal. The *joule* (j), a unit based on the C.G.S. system, is equal to 10^7 ergs. This being inconveniently small is generally multiplied by 1000, giving the *kilojoule* (J), which is, therefore, equal to 10^{10} ergs. The different units of heat energy are related as follows: —

$$1 \text{ cal.} = 0.001 \text{ Cal.} = 4.185 \text{ j} = 0.004185 \text{ J.}$$

Thermochemical Equations. Thermochemical data are expressed by writing the equation for the reaction and giving the value of ΔH for the reaction. For example

$$C + O_2 = CO_2 \qquad \Delta H = -94{,}400 \text{ calories.}$$

It will be remembered that ΔH represents the increase in heat content in passing from the reactants at the left of the equation to the reaction products at the right. The absolute values of the heat content are unknown and unnecessary. In the oxidation of carbon, heat is evolved and the heat content is thereby decreased, so that ΔH has a negative value. There is some confusion of sign because in the earlier work chemists designated heat evolved as positive, but now, in con-

formity with the notation of thermodynamics, heat evolved is generally regarded as negative. It will be so used in this book.

In writing equations, solids, liquids and gases are designated by (*s*), (*l*) and (*g*), respectively, and the preceding equation is written

$$C\ (s) + O_2\ (g) = CO_2\ (g) \qquad \Delta H = -94{,}400.$$

Sometimes these symbols are omitted when there is no chance of confusion.

Another convention used in the thermochemistry of solutions is the symbol aq. (*aqua* = water) signifying a large excess of water, so large that the addition of more water has no measurable effect on the temperature.

Thermochemical Measurements. Calorimeters are used for measuring the heat changes which accompany chemical reactions. In the most common type, the reaction is allowed to take place in a reaction chamber surrounded by a known quantity of water in an insulated vessel, and the rise in temperature is measured with a sensitive thermometer. The product of the rise in temperature and the total heat capacity of the water and calorimeter is a measure of the heat evolved. The heat capacity of the calorimeter is best obtained by measuring a reaction of known heat evolution, or by introducing a measured quantity of heat with an electrical heater. Corrections are necessary for the natural cooling of the heated calorimeter, unless the cooling is eliminated by experimental means. It is necessary to use reactions which proceed rapidly and definitely to completion, for otherwise the uncertainties in the cooling may introduce large errors. Heats of combustion in compressed oxygen are especially satisfactory in this respect. For this purpose the combustion calorimeter was devised by Berthelot. In this apparatus the essential feature is the so-called *combustion bomb*, shown at *B* in Fig. 85. This consists of a strong cylinder of a special acid-resisting alloy, which is furnished with a heavy threaded cover. The substance to be burned is placed in a platinum capsule fastened to appropriate supports, while a weighed piece of fine iron wire, the middle portion of which dips into the substance, is connected with electric terminals on the cover of the bomb. The cover is screwed down tight, and the bomb is filled with oxygen, under a pressure of from 20 to 25 atmospheres. The bomb is then submerged in the calorimeter. The mass of water in the calorimeter being known, and its temperature having been read, an electric current is passed through the iron ignition wire causing it to burn and thus ignite the substance. The rise in temperature, due to the combustion, is observed, and the quantity of heat evolved is calculated. Corrections must be

applied for the heat evolved from the combustion of the iron, and for the heat evolved from the oxidation of the nitrogen of the residual air in the bomb.

The calorimeter shown in Fig. 85 is of the adiabatic type, devised by Richards, in which the temperature of the jacketing water is constantly maintained at the same temperature as that of the water in the calorimeter itself, thereby eliminating the troublesome and uncertain cor-

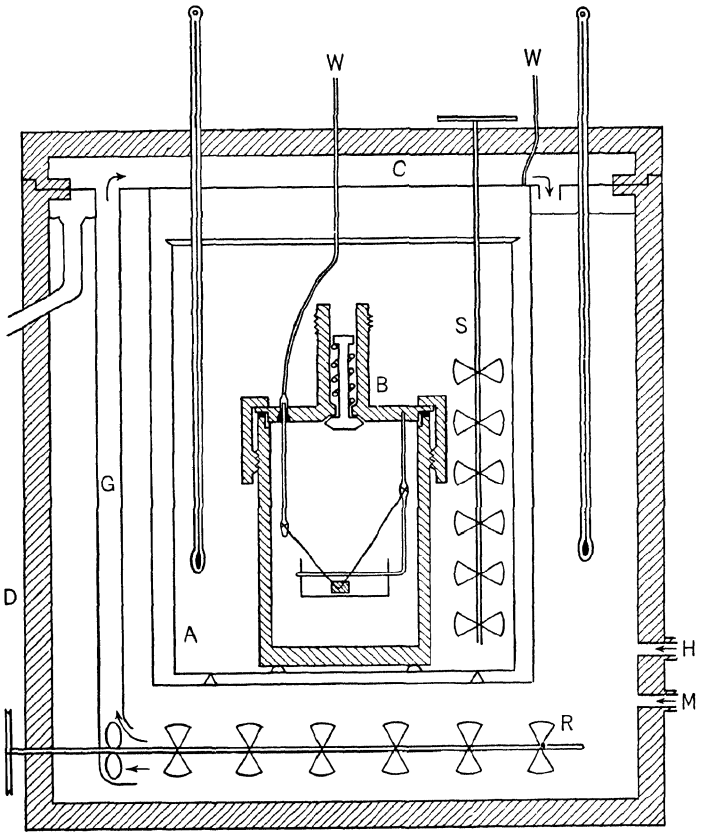


FIG. 85

rection for loss of heat by radiation. Water is circulated around the bomb *B*, in the inner vessel *A* by means of the stirrer *S*. In the outer jacket *D* water is forced through the tube *G* and the cover *C* by means of the stirrer *R*. The control of the temperature is accomplished with hot and cold water, the latter coming directly from the laboratory tap, and the former being furnished by a small heater (not shown in the

diagram). The hot and cold inlets, *H* and *M*, are so placed that the control cocks are easily operated by one hand. In other types the outer jacket is heated by electricity, or by mixing acid and alkali. The charge is exploded through the wires *WW*. This is Parr's calorimeter.

Law of Lavoisier and Laplace. In 1780, Lavoisier and Laplace, as a result of their thermochemical investigations, enunciated the following law: — The quantity of heat which is required to decompose a chemical compound is precisely equal to that which was evolved in the formation of the compound from its elements. This first law of thermochemistry will be seen to be a direct corollary of the law of the conservation of energy, first clearly stated by Mayer in 1842.

Law of Constant Heat Summation. A generalization of fundamental importance to the science of thermochemistry was discovered, in 1840, by Hess. He pointed out that the heat evolved in a chemical process is the same whether it takes place in one or in several steps. This is known as the law of constant heat summation. The truth of the law may be illustrated by the equality of the heat of formation of ammonium chloride in aqueous solution, when prepared in two different ways. Thus,

(*A*)

$NH_3\ (g) + HCl\ (g) = NH_4Cl\ (s)$	$\Delta H = -42{,}100$ cal.
$NH_4Cl\ (s) + aq. = NH_4Cl\ (aq.)$	$\Delta H = 3{,}900$ cal.
	$\Delta H = -38{,}200$ cal.

(*B*)

$NH_3\ (g) + aq. = NH_3\ (aq.)$	$\Delta H = -8{,}400$ cal.
$HCl\ (g) + aq. = HCl\ (aq.)$	$\Delta H = -17{,}300$ cal.
$NH_3\ (aq.) + HCl\ (aq.) = NH_4Cl\ (aq.)$	$\Delta H = -12{,}300$ cal.
	$\Delta H = -38{,}000$ cal.

It will be observed that the total amount of heat evolved in the formation and solution of ammonium chloride is the same, within the limits of experimental error, whether gaseous ammonia and hydrochloric acid are allowed to react, and the resulting product is dissolved in water, or whether the gases are each dissolved separately, and then allowed to react.

By means of the law of constant heat summation, it is possible to find indirectly the amount of heat developed, or absorbed, by any reaction, even though it is impossible to carry it out experimentally. For example, it is impossible to measure the heat evolved when carbon

burns to carbon monoxide. But the heat evolved when carbon monoxide burns to carbon dioxide, and also the heat evolved when carbon burns to carbon dioxide, can be accurately determined. The energy equations are as follows: —

$$C\ (s) + O_2\ (g) = CO_2\ (g) \qquad \Delta H = -94{,}400 \text{ cal.} \qquad (1)$$

$$CO\ (g) + \tfrac{1}{2}\ O_2\ (g) = CO_2\ (g) \qquad \Delta H = -67{,}700 \text{ cal.} \qquad (2)$$

Treating these equations algebraically, and subtracting equation (2) from equation (1), we have

$$C\ (s) + \tfrac{1}{2}\ O_2\ (g) = CO\ (g) \qquad \Delta H = -26{,}700 \text{ cal.}$$

Again, as a further illustration of the applicability of the law of Hess, we may take the calculation of the heat of formation of hydriodic acid from its elements, making use of the following energy equations: —

$$2\ KI\ (aq.) + Cl_2\ (g) = 2\ KCl\ (aq.) + I_2\ (s) \qquad \Delta H = -52.4 \text{ Cal.} \qquad (3)$$

$$2\ HI\ (aq.) + 2\ KOH\ (aq.) = 2\ KI\ (aq.) + 2\ H_2O\ (l) \qquad \Delta H = -27.4 \qquad (4)$$

$$2\ HCl\ (aq.) + 2\ KOH\ (aq.) = 2\ KCl\ (aq.) + 2\ H_2O\ (l) \qquad \Delta H = -27.4 \qquad (5)$$

$$2\ HI\ (g) + aq. = 2\ HI\ (aq.) \qquad \Delta H = -38.4 \qquad (6)$$

$$2\ HCl\ (g) + aq. = 2\ HCl\ (aq.) \qquad \Delta H = -34.6 \qquad (7)$$

$$H_2\ (g) + Cl_2\ (g) = 2\ HCl\ (g) \qquad \Delta H = -44.0. \qquad (8)$$

Adding equations (3) and (4),

$$Cl_2\ (g) + 2\ HI\ (aq.) + 2\ KOH\ (aq.) = 2\ KCl\ (aq.) + I_2\ (s) + 2\ H_2O\ (l) \qquad \Delta H = -79.8. \qquad (9)$$

Subtracting equation (5) from equation (9),

$$Cl_2\ (g) + 2\ HI\ (aq.) - 2\ HCl\ (aq.) = I_2\ (s) \qquad \Delta H = -52.4 \qquad (10)$$

or

$$Cl_2\ (g) + 2\ HI\ (aq.) = I_2\ (s) + 2\ HCl\ (aq.), \qquad \Delta H = -52.4. \qquad (11)$$

Adding equations (6) and (11),

$$2\ HI\ (g) + aq. + Cl_2\ (g) = I_2\ (s) + 2\ HCl\ (aq.), \qquad \Delta H = -90.8. \qquad (12)$$

Subtracting equation (7) from equation (12),

$$2\ HI\ (g) + Cl_2\ (g) - 2\ HCl\ (g) = I_2\ (s), \qquad \Delta H = -56.2$$

or

$$2\ HI\ (g) + Cl_2\ (g) = I_2\ (s) + 2\ HCl\ (g) \qquad \Delta H = -56.2. \qquad (13)$$

Subtracting equation (8) from equation (13),

$$2\ HI\ (g) - H_2\ (g) = I_2\ (s), \qquad \Delta H = -12.2 \qquad (14)$$

or

$$H_2\ (g) + I_2\ (s) = 2\ HI\ (g). \qquad \Delta H = 12.2. \qquad (15)$$

In a similar manner, practically any heat of formation may be calculated, provided the proper energy equations are combined.

Heats of Formation. Although it is not yet possible to know the absolute heat contents of chemical compounds, their *heats of formation* can be calculated by arbitrarily assuming that the heat content of the elements in their standard states is zero. For example, it follows from the reaction

$$C\ (s) + O_2\ (g) = CO_2\ (g) \qquad \Delta H = -94{,}400 \text{ cal.} \qquad (16)$$

that the heat of formation of carbon dioxide is $-94{,}400$, because 94,400 calories of heat is evolved when a mol of carbon dioxide gas is produced from the elements, and the elements are arbitrarily assigned a zero value. The heat content of the elements will vary, depending on their physical state, and it is conventionally agreed that they are to be taken in their naturally occurring state under one atmosphere pressure. In the example given, oxygen is a gas at atmospheric pressure and carbon is a solid. Unless the temperature is specified it is assumed to be 25° C. If two or more allotropic forms are stable at the specified temperature, it may be necessary to specify the form. In the case of carbon the diamond is sometimes taken for reference because it is more reproducible in its thermal properties than graphite.

The heats of formation of a number of metallic and non-metallic compounds are given in the accompanying table.

The calculation of heats of reaction may be greatly simplified by using the heats of formation when they are available. The change in heat content of a given reaction is obtained by subtracting the heats of formation of all the reacting materials from the heats of formation of all the products. The calculation is illustrated by the following reaction:

$$\begin{array}{ccccccc} MgCl_2\ (s) & + & 2\ Na\ (s) & = & 2\ NaCl\ (s) & + & Mg\ (s) \\ -153{,}200 & & +0 & & -2 \times 98{,}400 & & +0 \end{array} \qquad (17)$$

where the heats of formation are set under the compounds occurring in the equation. Then

$$\Delta H = (-2 \times 98{,}400 + 0) - (-153{,}200 + 0) = -43{,}600. \qquad (18)$$

In the same way heats of formation may be calculated from measured heats of reaction, as in the following example, where it is desired to find the heat of formation, x, of methane.

$$\begin{array}{ccccccc} CH_4\ (g) & + & 2\ O_2\ (g) & = & CO_2\ (g) & + & 2\ H_2O\ (l) \qquad \Delta H = -212{,}700 \\ x & + & 0 & & -94{,}400 + 2 \times (-68{,}380) & & \end{array} \qquad (19)$$

$$\Delta H = (-94{,}400 - 2 \times 68{,}380) - (x + 0)$$

$$= -212{,}700$$

$$x = -18{,}460. \qquad (20)$$

HEATS OF FORMATION*

(ΔH is given in Kg. calories at 20°)

Oxides	
Na_2O	− 99.3
K_2O	− 86.2
CaO	−151.8
BaO	−133.1
MgO	−145.9
ZnO	− 83.6
FeO	− 64 1
Fe_2O_3	−190.8
Fe_3O_4	−264 5
PbO	− 52.5
CuO	− 34.9
Ag_2O	− 6 95
HgO	− 21.8
Sulphides	
Na_2S	− 89 9
K_2S	− 88.3
CaS	−113.5
CuS	− 11.6
PbS	− 22.2
Chlorides	
$NaCl$	− 98.4
KCl	−108.4
$BaCl_2$	−202.7
$MgCl_2$	−153.2
$ZnCl_2$	− 99.5
$FeCl_2$	− 82.0
$FeCl_3$	− 96.4
$CuCl_2$	− 51.4
$AgCl$	− 30.6
$PbCl_2$	− 85.7
Bromides	
$NaBr$	− 86.4
KBr	− 94.0
$AgBr$	− 23.8
$PbBr_2$	− 66.3
Iodides	
NaI	− 69.5
KI	− 78.8
CuI	− 15.8
AgI	− 14.9
PbI_2	− 41.9
Nitrates	
$NaNO_3$	−112.5
KNO_3	−118.8
$Ba(NO_3)_2$	−238 2
$AgNO_3$	− 30.1
$Pb(NO_3)_2$	−116.3
Sulphates	
Na_2SO_4	−326.4
K_2SO_4	−338.3
$BaSO_4$	−345 5
$MgSO_4$	−301.3
$ZnSO_4$	−229.5
$CuSO_4$	−178.8
Ag_2SO_4	−166.0
$PbSO_4$	−214.6
(*Non-metallic Compounds*)	
HCl	− 21.8
HBr	− 8.65
HI	+ 5.93
H_2O (liq.)	− 68.4
H_2O (gas)	− 57.8
NH_3	− 10.9
SO_2	− 69.3
H_2SO_4	−189.8
N_2O	+ 17.0
NO	+ 21.5
HNO_3	− 42.4
CO	− 26.4
CO_2	− 94.4
CH_4	− 18.5
C_2H_2	+ 54.4
C_6H_6	+ 12.5

* The data are compiled from the International Critical Tables.

In a third example

$$CS_2\ (l) + 3\ O_2\ (g) = CO_2\ (g) + 2\ SO_2\ (g) \qquad \Delta H = -258{,}700$$
$$x + 0 \qquad -94{,}400 + -2 \times 69{,}300 \text{ cal.} \qquad (21)$$

The heat of formation of carbon disulphide x, is 25,700 calories. This heat of formation is positive; i.e., heat is absorbed when carbon disulphide is produced from its elements. Compounds of this type are called endothermic compounds in contradistinction to the exothermic compounds which are formed with the evolution of heat. They are much less common than the exothermic compounds and frequently they are unstable.

Heat of Solution. The thermal change accompanying the solution of 1 mol of a substance, in so large a volume of solution that no appreciable change in concentration is produced by the addition of the solute, is termed the differential heat of solution, or merely the *heat of solution.* The solution of salts is generally an endothermic process. This fact may be readily accounted for, on the hypothesis that considerable heat must be absorbed, as heat of fusion and heat of vaporization, before the solid salt can assume a condition in solution which closely resembles that of a gas.

HEATS OF SOLUTION AT 20°

Substance	Mols H_2O	ΔH	Substance	Mols H_2O	ΔH
HCl	200	−17.44 Cal.	NaBr	200	+ 0.19 Cal.
HBr	200	−19.92	$NaBr;2\,H_2O$	300	+ 4.71
HI	200	−19.24	NaI	200	− 1.41
NH_3	200	− 8.46	$NaI \cdot 2\,H_2O$	200	+ 4.01
H_2SO_4	200	−17.75	NaOH	200	− 9.94
HNO_3	200	− 7.48	$NaNO_3$	200	+ 5.01
NH_4Cl	200	+ 3.90	Na_2SO_4	400	− 0.55
NH_4NO_3	200	+ 6.34	$Na_2SO_4 \cdot 10\,H_2O$	400	+18.90
NaCl	200	+ 1.28	KCl	200	+ 4.44
$Ca(OH)_2$	2500	− 2.79	KBr	200	+ 5.03
$CaCl_2$	300	−17.99	KI	400	+ 5.12
$CaCl_2 \cdot 6\,H_2O$	400	+ 4.56	KOH	250	−13.29
$ZnSO_4$	400	−18.54	KNO_3	200	+ 8.46
$ZnSO_4 \cdot 7\,H_2O$	400	+ 4.28	K_2SO_4	400	+ 6.55
$CuCl_2$	600	−11.11	$CuSO_4$	800	−15.89
$CuCl_2 \cdot 2\,H_2O$	200	− 3.70	$CuSO_4 \cdot 5\,H_2O$	800	+ 2.85

Combination with the solvent evolves heat which may more than offset the cooling effect of solution. For example, when anhydrous calcium nitrate is dissolved in water there is an evolution of 4000

calories per mol, but when the tetrahydrate is dissolved there is an absorption of 7600 calories.

The difference between the heats of solution of the anhydrous and hydrated salts is termed the *heat of hydration.* The heats of solution in water of some of the more common compounds are given in the preceding table, the values being expressed in large calories. They may be compared with the influence of temperature on solubility (p. 157).

Heat of Dilution. The *heat of dilution* of a solution of specified concentration is the quantity of heat which is evolved, or absorbed, per mol of solute when the solution is greatly diluted. Beyond a certain dilution, further addition of solvent produces no thermal change. Those gases which obey Henry's law are practically the only substances which have no appreciable heats of solution, or dilution.

The following tables give the heats of dilution of several acids and bases.

HEATS OF DILUTION OF ACIDS (ΔH in Kg. Cal.)

Mols of H_2O Added	To HNO_3+H_2O	To $HCl+H_2O$	Mols of H_2O Added	To $H_2SO_4+H_2O$
1	−1.51	− 5.97	0.5	− 2.11
2	−2.44	− 7.98	1	− 3.30
4	−3.50	− 9.59	2	− 5.02
9	−4.04	−10.78	5	− 7.70
24	−4.23	−11.48	8	− 8.95
49	−4.18	−11.70	18	−10.43
99	−4.16	−11.90	48	−10.68
199	−4.16	−11.95	98	−10.90
399	−4.16	−12.00	198	−11.08
∞	−4.16	−12.07	398	−11.40
			798	−11.82
			1598	−12.30
			∞	−14.09

It is apparent, that as the dilution of these solutions is increased, the thermal effect produced by the addition of more solvent becomes less and less, and ultimately becomes zero. This is shown diagrammatically in Fig. 86, in which the abscissas represent the composition of the solutions, and the ordinates represent the corresponding heats of solution. The ordinates, An_1 and Bn_2, are the heats of solution of 1 mol of solute in n_1 and in n_2 mols of solvent.

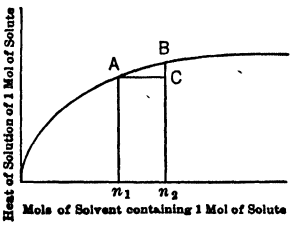


FIG. 86

These heats of solution are called *integral heats of solution*, and the difference between them is called the *integral heat of dilution*. In these examples the concentration changes during the solution process; the heat effect represented by BC is the integral heat of dilution corresponding to a change in concentration from n_1 to n_2. The *differential heats of solution* are more useful in theoretical work because they are more definite, and practical methods for their calculation will be given on p. **530**.

HEATS OF DILUTION OF BASES

Mols of Water Added	To $KOH+3\ H_2O$ ΔH	To $NaOH+3\ H_2O$ ΔH
2	−1500 cal.	−2130 cal.
4	−2100	−2980
6	−2360	−3080
22	−2700	−3090
47	−2730	−3080
97	−2740	−3000
197	−2750	−2950

Reactions at Constant Pressure and Constant Volume. When a reaction occurs at constant volume, no work is involved, but if the system is allowed to expand during the reaction it does work against the atmosphere and a smaller quantity of heat is evolved. If the system contracts, the heat of reaction at constant pressure is greater than that at constant volume by an amount equal to the work done on the system by the surroundings. In case the products and the reactants have the same volume the heats of reaction at constant pressure and constant volume are the same. These facts are summarized in the equation

$$\Delta H = \Delta U + p\,\Delta v = \Delta U + \Delta nRT, \qquad (22)$$

where ΔH is the heat of reaction at constant pressure, ΔU is the heat of reaction at constant volume, and $p\,\Delta v$ is the work done by the system. Since liquids and solids occupy very small volumes, the term $p\,\Delta v$ usually includes only the volumes of gases. The increase in the number of mols of gas is denoted by Δn, the number of mols of gaseous products minus the number of mols of gaseous reactants. At 25° C., RT has a value of 592 calories.

Heats of reaction are usually given for conditions of constant pressure because most reactions are studied at constant pressure. Heats

of combustion, however, are measured at constant volume, and equation (22) is useful in converting one into the other. For example, the combustion of methane takes place in accordance with the equation:

$$CH_4\,(g) + 2\,O_2\,(g) = CO_2\,(g) + 2\,H_2O\,(l) \quad \Delta U = -211{,}540. \quad (23)$$

The reaction is accompanied by a decrease of 2 mols of gas and, at 25° C., there will be an evolution of 1184 calories more heat at constant pressure than at constant volume.

$$\Delta H = \Delta U + p\,\Delta v = \Delta U + \Delta nRT = -211{,}540 + (-2) \times 1.987 \times 298 = -212{,}720 \text{ cal.}^* \quad (24)$$

Variation of Specific Heat with Temperature. In a previous chapter (p. 29), it has been shown that the value of the molar heat capacity of a monatomic gas, at constant pressure, is 5.0. According to the kinetic theory of gases, the heat capacity, at constant pressure, of any monatomic gas not only should be constant, but also should be independent of the temperature. This theoretical requirement has been fully confirmed by experiments carried out at temperatures ranging from −80° to 200°. The kinetic theory also indicates that the molar heat capacity of gases containing more than one atom per molecule should increase with the molecular complexity of the gas, and also with the temperature.

After testing a large number of empirical formulas which have been proposed from time to time, to express the variation of the molal heat capacity of gases with temperature, Lewis and Randall† have selected the following as the most trustworthy: —

For N_2, O_2, CO, NO, HCl, HBr, and HI,

$$C_p = 6.50 + 0.0010\,T \text{ cal.} \quad (25)$$

For H_2,

$$C_p = 6.50 + 0.0009\,T \quad (26)$$

For Cl_2, Br_2, and I_2,

$$C_p = 7.4 + 0.001\,T \quad (27)$$

For H_2O and H_2S,

$$C_p = 8.81 - 0.0019\,T + 0.00000222\,T^2 \quad (28)$$

For CO_2 and SO_2,

$$C_p = 7.0 + 0.0071\,T - 0.00000186\,T^2 \quad (29)$$

For NH_3,

$$C_p = 8.04 + 0.0007\,T + 0.0000051\,T^2. \quad (30)$$

* The accuracy of the experimental measurements is not sufficiently great to warrant expressing the last figure, i.e., 212,724.

† "Thermodynamics and the Free Energy of Chemical Substances," p. 80.

The use of these equations may be illustrated by calculating the quantity of heat required to raise the temperature of 1 mol of carbon dioxide from 50° to 100°. To calculate the quantity of heat absorbed, it is necessary to integrate the equation, $dH = C_p\,dT$, between the desired temperature limits, making use of equation (29) to determine the value of C_p, as follows:

$$\int_{323°}^{373°} dH = \int_{323°}^{373°} (7.0 + 0.0071\,T - 0.00000186\,T^2)\,dT,$$

$$\Delta H = H_{373} - H_{323} = 7.0\,(373 - 323) + \frac{0.0071}{2}(373^2 - 323^2)$$

$$- \frac{0.00000186}{3}(373^3 - 323^3)$$

$$= 350 + 123.54 - 11.28 = 462.26 \text{ cal.}$$

It will be observed that all of the foregoing formulas are derived for constant pressure conditions, but they may readily be transformed so as to apply to constant volume conditions, by subtracting 2 from the first term of each equation. On p. 27 it was shown that the molar heat capacity of a gas is greater at constant pressure than at constant volume by 2 calories. Equation (25) can then be written

$$C_v = 4.50 + 0.0010\,T. \tag{31}$$

Expressions for the influence of temperature on the specific heats of solids have been discussed on p. 81.

The influence of temperature on the specific heats of liquids is much more complicated. When the temperature of a liquid is raised, heat is absorbed in increasing the kinetic energy and the internal energy of the molecules as in the case of gases. Additional heat may be absorbed, also, in case complex molecules or polymerized molecules are broken down at the higher temperature. The heat capacity of liquids is usually greater than that of the corresponding solids and it often increases rapidly with temperature. The so-called "associated" liquids have higher heat capacities than the normal liquids. The mechanism of heat absorption is quite complicated, as evidenced by the fact that water shows a minimum in the specific heat-temperature curve at 30° C. and sulphur shows a sharp maximum at 160° corresponding to the heat of transition from one molecular species to another* (S_λ to S_μ).

The specific heats of a few organic liquids are given in the following table. The first term gives the heat capacity per gram extrapolated

* Lewis and Randall, J. Am. Chem. Soc., **33**, 476 (1911).

to 0° C.; the values at higher temperatures up to 60° may be obtained by substituting given temperatures for t.

SPECIFIC HEATS OF LIQUIDS*

Heptane	$0.4755 + 0.00142\,t$
Chloroform	$0.2250 + 0.000304\,t$
Toluene	$0.3726 + 0.000846\,t$
Nitrobenzene	$0.3306 + 0.000452\,t$
Ethyl alcohol	$0.5068 + 0.00286\,t + 5.4 \times 10^{-6}\,t^2$

* Williams and Daniels, J. Am. Chem. Soc., **46**, 904 (1924).

Variation of Heat of Reaction with Temperature. If a chemical reaction is allowed to take place first at the temperature T_1 and then at the temperature T_2, the amounts of heat developed in the two cases will be found to be quite different. Let us assume that the initial state of the system is represented by the point A, in Fig. 87, and that the final state is represented by the point B. It is evident that we can pass from A to B by two independent paths, namely AmB and AnB. According to the first law of thermodynamics the net absorption, or evolution of heat, must be the same by either path.

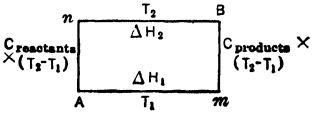


FIG. 87

Along the path AmB the reaction takes place at temperature T_1 with the heat change ΔH_1 and the products are then heated from T_1 to T_2 along mB. The heat absorbed in this last stage is the heat capacity of the products multiplied by the temperature rise, $C_{\text{products}}\,(T_2 - T_1)$.

Along the path AnB the reactants are first heated to temperature T_2, and the heat absorbed is the heat capacity of the reactants multiplied by the temperature rise, $C_{\text{reactants}}\,(T_2 - T_1)$. The reaction is then allowed to take place at temperature T_2 with the heat change ΔH_2. Then

$$\Delta H_1 + C_{\text{products}}\,(T_2 - T_1) = \Delta H_2 + C_{\text{reactants}}\,(T_2 - T_1) \qquad (32)$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_{\text{products}} - C_{\text{reactants}} = \Delta C_p, \qquad (33)$$

where ΔC_p is the increase in heat capacity at constant pressure. When heat is evolved, ΔH has a negative sign and

$$\frac{(-\Delta H_1) - (-\Delta H_2)}{T_2 - T_1} = \frac{\text{Heat evolved at } T_1 - \text{Heat evolved at } T_2}{T_2 - T_1} = \Delta C_p. \qquad (34)$$

This relation was discovered by Kirchhoff.

In other words, if the heat capacity increases during a reaction the evolution of heat becomes less as the temperature is raised.

In this equation it is assumed that the heat capacities do not change when the temperature is changed. The more general case, where the heat capacities do change, is handled by integration.

For very small temperature increases at constant pressure

$$\frac{d(\Delta H)}{dT} = \Delta C_p \tag{35}$$

where ΔH represents a single quantity, and

$$\int_{\Delta H_1}^{\Delta H_2} d\,(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p\, dT. \tag{36}$$

The use of equation (33) may be illustrated by calculating the heat of combustion of hydrogen at 110° from a knowledge of the heat of reaction at 18°.

$$2\ H_2\ (g) + O_2\ (g) = 2\ H_2O\ (l) \qquad \Delta H_{291} = -136{,}710 \text{ cal.} \tag{37}$$

The reaction takes place at constant pressure, and the *average* molar heat capacities over this temperature are as follows:

Oxygen = 6.84;	Water vapor = 8.42;
Hydrogen = 6.80;	Liquid water = 18.

The heat of reaction to give liquid water at 100° C. is obtained by substituting in equation (33):

$$\frac{\Delta H_{373} - (-136{,}710)}{373 - 291} = (2 \times 18) - [(2 \times 6.80) + 6.84] = 15.56$$

$$\Delta H_{373} = (15.56 \times 82) - 136{,}710 = -135{,}430.$$

If water vapor is produced instead of liquid water the heat evolved at 100° C. will be less by an amount equal to the heat of vaporization, which is 36 × 539 or 19,400 calories.

$$2\ H_2O\ (l) = 2\ H_2O\ (g). \qquad \Delta H = 19{,}400$$

$$\Delta H_{373} = -135{,}430 + 19{,}400 = -116{,}030 \text{ cal.}$$

The heat of reaction at 110° may now be calculated from the heat capacities of steam, hydrogen and oxygen using equation (33):

$$\frac{\Delta H_{383} - (-116{,}030)}{383 - 373} = (2 \times 8.42) - (2 \times 6.80 + 6.84) = -3.60.$$

$$\Delta H_{383} = (-3.60 \times 10) - 116{,}030 = -116{,}070 \text{ cal.}$$

Heat of Combustion. The heat evolved during the complete oxidation of unit mass of a substance is termed its *heat of combustion.*

The unit of mass commonly chosen in all physicochemical calculations is the mol. An enormous amount of experimental work has been done on the determination of the heats of combustion of a large number of chemical compounds by Thomsen,* Berthelot,† Langbein,‡ Richards,§ and others. The accompanying table gives the heats of combustion of several organic compounds determined with extreme accuracy by Richards and Davis.

HEATS OF COMBUSTION AT CONSTANT VOLUME

Substance	Heat of Combustion per Mol ΔU
Sucrose	−1,349,400 cal.
Benzoic acid	− 771,550
Naphthalene	−1,231,600
Benzene	− 781,850
Toluene	− 935,230
Tertiary butyl benzene	−1,399,800
Cyclohexanol	− 889,300
Di-isoamyl	−1,612,600
Methyl alcohol	− 170,610
Ethyl alcohol	− 327,040
Propyl alcohol	− 485,800
Butyl alcohol	− 638,330
Isobutyl alcohol	− 637,140

It has been observed that the average change in the molar heat of combustion, in any ascending homologous series of hydrocarbons, is −153,500 calories for each CH_2 group added. It was successfully pointed out by Thornton,¶ that the molar heat of combustion of any saturated hydrocarbon is approximately −52,700 calories for each atomic weight of oxygen required to burn it. For example, the complete combustion of methane may be represented by the equation,

$$CH_4\ (g) + 2\ O_2\ (g) = CO_2\ (g) + 2\ H_2O\ (l)$$

since 4 atomic weights of oxygen are required to burn 1 mol of methane, it follows, according to Thornton's rule, that the heat of combustion

* Thermochemische Untersuchungen, 4 Vols.

† Essai de Mécanique Chimique, Thermochimie, Donées et Lois Numériques.

‡ J. prakt. Chem., 1885 to 1895.

§ Richards and Barry, J. Am. Chem. Soc., **37**, 993 (1915); Richards and Davis, ibid., **42**, 1599 (1920).

¶ Phil. Mag., **33**, 196 (1917).

of the latter must be $4 \times (-52{,}700) = -210{,}800$ calories, a value which is in good agreement with that obtained by direct experiment.

A number of other interesting relations between heats of combustion of compounds and their differences in composition have been discovered, but these cannot be taken up at this time. It has also been pointed out that the heat of combustion of organic compounds is conditioned not only by their composition, but also by their molecular constitution.*

Some exceedingly interesting and important results have been obtained with the different allotropic forms of the elements. For example, when equal masses of the three common allotropic forms of carbon are burned successively in oxygen, the amounts of heat evolved are found to be quite different, as is shown by the following energy equations:

C (*s*) diamond	$+ O_2\ (g) = CO_2\ (g)$	$\Delta H = -94.3$ Cal.
C (*s*) graphite	$+ O_2\ (g) = CO_2\ (g)$	$\Delta H = -94.8$ Cal.
C (*s*) amorphous	$+ O_2\ (g) = CO_2\ (g)$	$\Delta H = -97.65$ Cal.

It is apparent that amorphous carbon contains the greatest amount of energy of any one of the three allotropic modifications and, therefore, if this form of carbon were to undergo transformation into the diamond, the reaction would be accompanied by the evolution of $\Delta H = -97.65 - (-94.3) = -3.35$ Calories. In like manner, the allotropic forms of both sulphur and phosphorus have different heats of combustion. The following equations express the differences in internal energy between the allotropic forms of the two elements:

S (monoclinic) = S (rhombic)	$\Delta H = -0.069$ Cal.
P (white) = P (red)	$\Delta H = -4.30$ Cal.

When the same substance is burned in oxygen, and then in ozone, it is found that more heat is evolved in ozone than in oxygen. The energy equation expressing the change of ozone into oxygen may be written thus,

$$O_3\ (g) = 1\tfrac{1}{2}\ O_2\ (g) \qquad \Delta H = -34.4 \text{ Cal.}$$

All the above facts illustrate the general principle that larger amounts of energy are associated with unstable than with stable forms.

Thermoneutrality of Salt Solutions. In addition to the law of constant heat summation, Hess discovered two other important laws of thermochemistry, viz., the law of thermoneutrality of salt solutions,

* Redgrove, Chem. News, **116**, 37 (1917); Swietoslawski, J. Am. Chem. Soc., **42**, 1312 (1920). Kharasch and Sher, J. Phys. Chem., **29**, 625 (1925).

and the law governing the neutralization of acids by bases.* When two dilute salt solutions are mixed there is neither evolution nor absorption of heat. Thus, when dilute solutions of sodium nitrate and potassium chloride are mixed, there is no thermal effect. The energy equation may be written as follows: —

$$NaNO_3\ (aq.) + KCl\ (aq.) = NaCl\ (aq.) + KNO_3\ (aq.) \qquad \Delta H = 0.$$

The explanation of the phenomenon of thermoneutrality was furnished by the theory of electrolytic dissociation. When the above equation is written in the ionic form, it becomes

$$Na^+ + NO_3^- + K^+ + Cl^- = Na^+ + Cl^- + K^+ + NO_3^-.$$

From this it is apparent that the same ions exist on both sides of the equation, and in reality no reaction takes place.

There are numerous exceptions to the law of thermoneutrality, but these also can be satisfactorily accounted for by means of the theory of electrolytic dissociation. All those salts, the behavior of which in dilute solution is contrary to the law, are found to be only partially ionized and, therefore, when their solutions are mixed, a chemical reaction actually occurs. The exceptions must be considered as furnishing additional evidence in favor of the theory of electrolytic dissociation.

Heat of Neutralization. Hess also discovered that, when dilute solutions of equivalent quantities of strong acids and strong bases are mixed, practically the same amount of heat is evolved in each case. The following energy equations may be considered as typical examples of such neutralizations:

$$HCl\ (aq.) + NaOH\ (aq.) = NaCl\ (aq.) + H_2O \qquad \Delta H = -13.68\ Cal.$$
$$HNO_3\ (aq.) + NaOH\ (aq.) = NaNO_3\ (aq.) + H_2O \qquad \Delta H = -13.69\ Cal.$$
$$HCl\ (aq.) + KOH\ (aq.) = KCl\ (aq.) + H_2O \qquad \Delta H = -13.93\ Cal.$$
$$HNO_3\ (aq.) + KOH\ (aq.) = KNO_3\ (aq.) + H_2O \qquad \Delta H = -13.87\ Cal.$$
$$HCl\ (aq.) + LiOH\ (aq.) = LiCl\ (aq.) + H_2O \qquad \Delta H = -13.70\ Cal.$$

Here, again, it would be difficult to explain the phenomenon without the theory of electrolytic dissociation. By means of this theory, however, the explanation is both simple and satisfactory. If MOH and HA represent any strong base and any strong acid, respectively, then when equivalent amounts of these are dissolved in water, each solution being largely diluted to the same volume, the reaction may be written thus:

$$M^+ + OH^- + H^+ + A^- = M^+ + A^- + H_2O \qquad \Delta H = -13.8\ Cal.$$

Disregarding the ions which occur on both sides of the equality sign, we have $OH^- + H^+ = H_2O \qquad \Delta H = -13.8\ Cal.$

* Pogg. Ann., **50**, 385 (1840).

It thus appears that the neutralization of a strong acid by a strong base in dilute solution consists solely in the combination of hydrogen and hydroxyl ions to form undissociated water. The heat of this ionic reaction is −13.8 Calories. The heat of formation of water from its ions must not be confused with the heat of formation of water from its elements.

When weak acids or weak bases are neutralized by strong bases or strong acids, respectively, or when weak acids are neutralized by weak bases, the heat of neutralization may differ widely from −13.8 Calories. This is shown by the following thermochemical equations:

$$H\cdot COOH\ (aq.) + NaOH\ (aq.) = H\cdot COONa\ (aq.) + H_2O \qquad \Delta H = -13.40\ \text{Cal.},$$

$$CHCl_2\cdot COOH\ (aq.) + NaOH\ (aq.) = CHCl_2\cdot COONa\ (aq.) + H_2O \qquad \Delta H = -14.83\ \text{Cal.},$$

$$H\cdot COOH\ (aq.) + NH_4OH\ (aq.) = H\cdot COONH_4\ (aq.) + H_2O \qquad \Delta H = -11.90\ \text{Cal.},$$

$$HCN\ (aq.) + NaOH\ (aq.) = NaCN\ (aq.) + H_2O \qquad \Delta H = -2.90\ \text{Cal.}$$

As will be seen, the heat of neutralization may be either greater or less than 13.8 Calories. The exceptions to the rule, that the heat of neutralization of an acid by a base is constant, are readily explained by the theory of electrolytic dissociation. Suppose a weak acid to be neutralized by a strong base. According to the dissociation theory, the acid is only slightly dissociated and, therefore, yields a comparatively small number of hydrogen ions to the solution. The base, on the other hand, is completely dissociated into hydroxyl and metallic ions. Therefore, as many hydroxyl ions disappear as there are free hydrogen ions with which they can combine, to form water. When the equilibrium between the acid and the products of its dissociation has been thus disturbed, it undergoes further dissociation, and the resulting hydrogen ions immediately combine with the free hydroxyl ions of the base. This process continues, until all the hydroxyl ions of the base have been neutralized. It is evident that the total thermal effect, in this case, must be equal to the algebraic sum of the heat of dissociation of the weak acid, which may be positive or negative, and the heat of formation of water from its ions. A similar explanation holds for the neutralization of a weak base by a strong acid, or for the neutralization of a weak acid by a weak base.

The approximate value of the heat of dissociation of a weak acid, or a weak base may be estimated, provided its heat of neutralization

by a strong base or strong acid is known. For example, in the equation given above,

$$HCN\ (aq.) + NaOH\ (aq.) = NaCN\ (aq.) + H_2O \quad \Delta H = -2.90\ Cal.$$

the difference between -2.9 and -13.8 or $+10.9$ Calories represents, approximately, the heat absorbed in the dissociation of hydrocyanic acid. Since the acid is initially slightly dissociated in dilute solution, it is apparent that, in order to obtain the true heat of dissociation, we must add to 10.9 Calories the thermal value of the dissociation of that portion of the acid which has already become ionized.

It has been shown by Wörmann* that the average value of 13.8 kilogram-calories per mol of water formed does not remain constant at temperatures much above or below room temperature. The following table contains some of Wörmann's data.

HEATS OF NEUTRALIZATION AT DIFFERENT TEMPERATURES

Temperature	Concentration of Acid and Base	KOH + HCl ΔH	NaOH + HCl ΔH
0°	0 25	−14,707 cal.	−14,580 cal.
0	0.10	−14,709	−14.604
6	0.25	−14,473	−14,352
6	0.1875	−14,463	−14,359
6	0.125	−14,448	−14,331
18	0.25	−13,937	−13,714
18	0.125	−13,957	−13,693
18	0.05	−13,887	−13,631
32	0.25	−13,155	−12,974
32	0.125	−13,171	−12,922
32	0.05	−13,160	−12,980

Heat of Ionization. Since -13.8 Calories is the heat of formation of water from its ions, this must also be the thermal equivalent of the energy required to dissociate 1 mol of water into its ions. It must be remembered that the dissociated molecule of water must be mixed with a very large volume of undissociated water, in order that the dissociation may be permanent. Reference to the table of heats of formation (p. 251), will show that 68.4 Calories is evolved in forming 1 mol of water from its elements. Hence, it follows that $-68.4 + 13.8 = -54.6$ Calories is the heat of formation of one equivalent of hydrogen and hydroxyl ions. It has been shown that an extremely small amount of energy is necessary to ionize hydrogen when it is dissolved in water. It is evident, therefore, that -54.6 Calories is a

* Ann. der Physik, **18**, 775 (1905).

close approximation to the heat of formation of one equivalent of hydroxyl ions.

On the assumption that the heat of ionization of gaseous hydrogen in solution is zero, the values of the other ionic heats of formation may be computed. For example, the heat of formation of KOH (aq.) is −114.9 Calories. The heat of formation of potassium ions must be, −114.9 + 54.6 = −60.3 Calories. In like manner, the heat of formation of KCl (aq.) is −99.9 Calories; hence the heat of formation of chlorine ions must be, −99.9 + 60.3 = −39.6 Calories. The accompanying table of ionic heats of formation has been calculated in this manner.

HEAT OF FORMATION OF IONS

Ion	Heat of Formation ΔH	Ion	Heat of Formation ΔH
Hydrogen	0.0	Copper (ic)	+ 16.5
Potassium	− 60.3	Copper (ous)	+ 16.0
Sodium	− 57.6	Mercury (ous)	+ 20.1
Lithium	− 66.4	Silver	+ 24.9
Ammonium	− 31.7	Lead	− 0.5
Magnesium	−110.0	Tin (ous)	− 2.4
Calcium	−129.5	Chloride	− 39.6
Aluminum	−126.4	Bromide	− 28.6
Manganese	− 48.0	Iodide	− 13.3
Iron (ous)	− 20.8	Sulphate	−211.3
Iron (ic)	− 9.6	Sulphite	−146.8
Cobalt	− 16.5	Nitrite	− 25.6
Nickel	− 15.3	Nitrate	− 49.8
Zinc	− 36.6	Carbonate	−161.0
Cadmium	− 17.4	Hydroxyl	− 54.6

REFERENCES

Treatise on Physical Chemistry, Chapter VI. Taylor.
Thermochemistry. Thomsen, translated by Burke.
Calorimetry. White.
The Specific Heats of Gases. Partington and Schilling.
Experimental Physical Chemistry, Chapters V and XXII. Daniels, Mathews and Williams.

PROBLEMS

1. In an adiabatic calorimeter the combustion of 0.6680 gram of naphthalene causes the temperature to rise 3.182°. The heat capacity of the calorimeter and water is 2019 grams. Neglecting corrections for the oxidation of the ignition wire and the residual nitrogen, what is the heat of combustion of naphthalene per mol? The molecular weight of napthalene is 128.06. *Ans.* 1231 Cal.

2. In an adiabatic calorimeter, the combustion of 1.5928 gram of sugar ($C_{12}H_{22}O_{11}$) produced a temperature rise of 2.869°. The molar heat of combustion of sugar is 1349.6 Cal. (*a*) What is the total heat capacity of the water and the calorimeter? (*b*) If the calorimeter contains 1830 grams of water (specific heat = 1.0), what is the effective heat capacity of the calorimeter? In this problem corrections for the oxidation of the wire and residual nitrogen may be neglected.

3. The heats of solution of Na_2SO_4, $Na_2SO_4 \cdot H_2O$, and $Na_2SO_4 \cdot 10\ H_2O$ are -0.46, $+1.9$ and $+18.76$ Cal. respectively. What are the heats of hydration of Na_2SO_4; (*a*) to monohydrate, (*b*) to decahydrate?

Ans. (*a*) $\Delta H = -2.36$ Cal. (*b*) $\Delta H = -19.22$ Cal.

4. The heat of solution of $BaCl_2$ is -2070 cals. and the heat of hydration to $BaCl_2 \cdot 2\ H_2O$ is -6970 cals. What is the heat of solution of $BaCl_2 \cdot 2\ H_2O$?

5. From the following data calculate the heat of formation of HNO_2(aq.)

$NH_4NO_2(s) = N_2(g) + 2\ H_2O(l)$	$\Delta H = -71.77$ Cal.
$2\ H_2(g) + O_2(g) = 2\ H_2O(l)$	$\Delta H = -136.72$ Cal.
$N_2(g) + 3\ H_2(g) + \text{aq.} = 2\ NH_3\text{(aq.)}$	$\Delta H = -40.64$ Cal.
$NH_3\text{(aq.)} + HNO_2\text{(aq.)} = NH_4NO_2\text{(aq.)}$	$\Delta H = -9.110$ Cal.
$NH_4NO_2(s) + \text{aq.} = NH_4NO_2\text{(aq.)}$	$\Delta H = 4.75$ Cal.
Ans. $\frac{1}{2}\ H_2(g) + \frac{1}{2}\ N_2(g) + O_2(g) + \text{aq.} = HNO_2\text{(aq.)}$	$\Delta H = -30.77$ Cal.

6. Calculate the heat of formation of sulphur trioxide from the following data:

$PbO + S + \frac{3}{2}\ O_2 = PbSO_4$	$\Delta H = -165.6$ Cal.
$PbO + H_2SO_4 \cdot 5\ H_2O = PbSO_4 + 6\ H_2O$	$\Delta H = -23.3$ Cal.
$SO_3(s) + 6\ H_2O = H_2SO_4 \cdot 5\ H_2O$	$\Delta H = -41.1$ Cal.

7. Calculate ΔH for the reaction

$$CO_2(g) + 4\ H_2(g) = CH_4(g) + 2\ H_2O(g)$$

from the heats of formation (page 251). *Ans.* $\Delta H = -39.7$ Cal.

8. Compute ΔH for the reaction

$CO_2(g) + H_2(g) = H_2O(g) + CO(g)$, from the heats of formation.

9. Calculate the heat of formation of NH_4Cl from the facts that one mol of ammonia combines with one mol of hydrochloric acid gas to form ammonium chloride with the evolution of 42,100 calories ($\Delta H = -42{,}100$ cal.) and that the heat of formation of ammonia is $-10{,}900$ and the heat of formation of hydrochloric acid is $-21{,}800$.

Ans. $\Delta H = -74{,}800$ cal.

10. For the heat of combustion of naphthalene ($C_{10}H_8$), $\Delta H = -1231.6$ Cal. The heats of formation of carbon dioxide and water may be obtained from tables (page 251). What is the heat of formation of naphthalene?

11. Compute the heat evolved, per mol of lead, in the smelting of lead

$$PbS + O_2 = Pb + SO_2$$

from the data on the heats of formation and the equations

(*a*) $PbS + 2\ O_2 = PbSO_4$ and $PbSO_4 + PbS = 2\ Pb + 2\ SO_2$.

Check the calculation using the equations

(*b*) $2\ PbS + 3\ O_2 = 2\ PbO + 2\ SO_2$ and $2\ PbO + PbS = 3\ Pb + SO_2$.

12. According to Thomsen the integral heat of solution of 1 mol of H_2SO_4 in n mols of water is given by the formula:

$$\Delta H_{\text{solution}} = \frac{-17{,}860\ n}{n + 1.798} \text{ calories.}$$

Calculate ΔH for the following reactions:

(*a*) Solution of 1 mol of H_2SO_4 in 5 mols of water.

(*b*) Solution of 1 mol of H_2SO_4 in 10 mols of water.

(*c*) Solution of 1 mol of sulphuric acid in a large excess of water, 100,000 mols for example.

(*d*) Addition of a large excess of water to a solution containing 1 mol of sulphuric acid in 5 mols of water.

(*e*) Addition of 5 mols of water to a solution containing 1 mol of sulphuric acid in 5 mols of water. *Ans.* (*a*) −13,136 calories.

13. (*a*) Differentiate the formula given in the preceding problem (#12) and obtain an expression for the rate of change of heat of solution with addition of water.

(*b*) What is the differential heat of solution of sulphuric acid in water in a solution containing 1 mol of sulphuric acid in 5 mols of water?

14. With the formula given in problem #12 calculate ΔH for various values of n (1, 5, 10 and 15), plot the data and draw a smooth curve. Draw a tangent to the curve where $n = 5$ and determine its slope. Compare this differential heat of solution with the value calculated in problem #13.

15. The equation $CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$, represents the combustion of methane. At 27° C, when liquid water is formed, how great is the difference between the heat of reaction at constant pressure and the heat of reaction at constant volume? Which is the larger?

16. Calculate the heat of combustion of naphthalene at 17° at constant volume. When naphthalene is oxidized at constant pressure $\Delta H = -1231.6$ Cal.

17. (*a*) From some of the following thermochemical equations at 17° and at constant pressure, calculate the heat evolved at constant pressure in the reaction

$$3\,C_2H_2(g) = C_6H_6(l)$$

$C(s) + O_2(g) = CO_2(g)$	$\Delta H = -96.96$ Cal.
$2\,H_2(g) + O_2(g) = 2\,H_2O(l)$	$\Delta H = -136.72$ Cal.
$2\,C_6H_6(l) + 15\,O_2(g) = 12\,CO_2(g) + 6\,H_2O(l)$	$\Delta H = -1598.7$ Cal.
$2\,C_2H_2(g) + 5\,O_2(g) = 4\,CO_2(g) + 2\,H_2O(l)$	$\Delta H = -620.1$ Cal.

(*b*) Calculate the heat evolved when the reaction is carried out at constant volume.

18. Calculate with the help of integral calculus, the quantity of heat required to raise the temperature of 1 mol of steam at constant pressure, from 100° to 200°.

19. Calculate the number of calories required to raise the temperature of 60 grams of nitric oxide, at constant volume, from 100° to 150°. *Ans.* 490 cal.

20. How many calories of heat are required to raise 1000 grams of ethanol from 10° to 50° C?

21. The mean specific heat of benzene (C_6H_6) from 17° to 75° is 0.3841 cal/gram. The heat capacity of acetylene is 10.43 cal./mol.

For the reaction, $3\,C_2H_2 = C_6H_6$, at 17° $\Delta H = -130.8$.

What is the value of ΔH at 75°?

22. The heat of fusion of water at 0° is 333.6 joules per gram. The specific heat of ice is 0.492. The specific heat of water is 1. What is the heat of fusion at −7°?

23. The heat of formation of 2 HBr from its elements is −16,880 cal. at 18°. The mean specific heats at constant pressure of the two reacting gases and their product are as follows: — $H_2 = 3.409$, $Br_2 = 0.0553$, HBr = 0.0820. Calculate the heat of formation of HBr at 150° C.

24. Determine the heat of reaction between hydrogen and oxygen at 200° as shown on page 258, but make the calculation more exact by using formulas which allow for the changes in heat capacities with temperature.

25. Compute the molal heat of combustion of trimethylmethane by Thornton's rule.

CHAPTER XII

HOMOGENEOUS EQUILIBRIUM

Historical Introduction. Ever since the metaphysical speculations of the Greeks, who endowed the atoms with the instincts of love and hate, the nature of chemical affinity has been under discussion. Newton's discovery of the law of gravitation led him to consider the attraction between atoms, and the attraction between large masses of matter as manifestations of the same force. Although Newton found that chemical attraction does not follow the law of the inverse square, yet his suggestion exerted a profound influence upon the minds of his contemporaries.

Geoffroy and Bergmann arranged chemical substances in the order of their displacing power. Thus, if we have three substances, A, B, and C, and the attraction between A and B is greater than that between A and C, then when B is added to AC, it will completely displace C, as indicated by the following equation:

$$AC + B = AB + C.$$

These investigators overlooked a factor of fundamental importance in conditioning chemical reactivity, namely, the influence of concentration. The importance of the relative amounts of the reacting substances in determining the course of a reaction was first clearly recognized by Wenzel, in 1777. It remained for Berthollet,* however, to point out the significance of the views advanced by Wenzel. His first paper on this subject was published in 1799, while acting as a scientific adviser to Napoleon on his Egyptian expedition. Under ordinary conditions, sodium carbonate and calcium chloride react according to the equation,

$$Na_2CO_3 + CaCl_2 = 2\,NaCl + CaCO_3.$$

This reaction was found to proceed nearly to completion. Berthollet observed the deposits of sodium carbonate on the shores of certain saline lakes in Egypt, and pointed out that this salt is produced by the reversal of the above reaction, the large excess of sodium chloride in solution in the water of the lakes conditioning the course of the reaction.

* Essai de statique chimique.

In 1862, an important contribution to our knowledge of the effect of concentration on the course of a chemical reaction was made by Berthelot and Péan de St. Gilles.* They investigated the formation of esters from alcohols and acids. The reaction between ethyl alcohol and acetic acid is represented by the equation,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

Starting with equivalent quantities of alcohol and acid, the reaction proceeds until about two-thirds of the reacting substances have been converted into ester and water. In like manner, if equivalent quantities of ethyl acetate and water are brought together, the reaction proceeds in the direction indicated by the lower arrow, until about one-third of the original substances have been converted into acid and alcohol. In other words, the reaction is reversible, a condition of equilibrium resulting when the speeds of the two reactions, indicated by the upper and lower arrows, become equal. If now a fixed amount of acid is taken, say 1 equivalent, and the quantity of alcohol is varied, a corresponding displacement of the equilibrium follows. The following table gives the results, obtained by Berthelot and Péan de St. Gilles, for ethyl alcohol and acetic acid. The first and third columns give the number of equivalents of alcohol to 1 equivalent of acetic acid, and the second and fourth columns give the percentage of acetic acid converted into ester.

EQUILIBRIUM IN REACTION BETWEEN ACETIC ACID AND ETHYL ALCOHOL

Equivalents of Alcohol	Per cent Acid Converted	Equivalents of Alcohol	Per cent Acid Converted
0.2	19.3	2.0	82 8
0.5	42.0	4.0	88.2
1.0	66.5	12.0	93.2
1.5	77.9	50.0	100.0

The effect of increasing the concentration of alcohol on the course of the reaction is clearly shown in this table.

The Law of Mass Action. While the influence of the relative concentrations of the reacting substances in conditioning chemical reactions was thus fully established, it was not until 1867 that the law governing the action of mass was accurately formulated.

* Ann. chim. phys. [3], **65**, 385; **66**, 5; **68**, 225 (1862–1863).

In that year, Guldberg and Waage,* two Scandinavian investigators, enunciated the law of mass action as follows: — *The rate, or speed, of a chemical reaction is proportional to the active masses of the reacting substances present at that time.* Guldberg and Waage defined the term "active mass" as the molecular concentration of the reacting substances. It is to be carefully noted that the amount of chemical action is not proportional to the actual quantities of the substances present, but rather to the amounts present in unit volume.

In general a reversible reaction like that between alcohol and acetic acid may be written

$$A + B + \ldots \rightleftarrows G + H + \ldots \tag{1}$$

and the concentrations, c, of each constituent may be written c_A, c_B, c_G, c_H. According to the mass law, the speed with which A and B react depends on the concentrations of A and B. Then

$$\text{Speed}_{\text{forward reaction}} \propto c_A \cdot c_B, \text{ or } \text{Speed}_{\text{forward reaction}} = k_1 c_A \cdot c_B,$$

where k_1 is the velocity constant. This speed is greatest when A and B are first mixed together and it gradually decreases as these reactants are used up.

The products of the reaction, G and H, react to give A and B, and the rate of this reaction also depends on the concentration of G and H. Then

$$\text{Speed}_{\text{reverse reaction}} = k_2 c_G \cdot c_H.$$

When more than 1 mol of a substance is involved in a reaction, each mol must be considered separately in the mass law. In the more general equation, each of the substances in the equation has a coefficient, 1, 2 or 3, etc.

Equation (1) may be rewritten

$$aA + bB + \ldots \rightleftarrows gG + hH + \ldots \tag{2}$$

showing that a mols of A and b mols of B react to give g mols of G and h mols of H. At equilibrium

$$k_1 c^a{}_A \cdot c^b{}_B \ldots = k_2 c^g{}_G \cdot c^h{}_H \ldots$$

and

$$K_c = \frac{k_1}{k_2} = \frac{c^g{}_G \cdot c^h{}_H \ldots}{c^a{}_A \cdot c^b{}_B \ldots} \tag{3}$$

Equilibrium Constants. Since, at any one temperature, the partial pressure of a substance is proportional to its concentration in the gas

* Études sur les affinités chimiques, J. prakt. Chem. [2], **19**, 69 (1879).

phase, we may write equation (3) in the following manner:

$$K_p = \frac{p^g_G \cdot p^h_H \cdot \cdot \cdot}{p^a_A \cdot p^b_B \cdot \cdot \cdot} \tag{4}$$

In gaseous equilibria this is often a more convenient form of the equation.

The concentrations of gases are expressed in mols per liter, and the partial pressures are usually given in atmospheres (sometimes in millimeters of mercury). The relation between the two equilibrium constants, K_c and K_p, can be determined easily since $c = 1/v = p/RT$ and equation (5) is obtained by substituting this value of c into equation (3)

$$K_c = \frac{\left(\frac{p_G}{RT}\right)^g \left(\frac{p_H}{RT}\right)^h}{\left(\frac{p_A}{RT}\right)^a \left(\frac{p_B}{RT}\right)^b} = \left(\frac{1}{RT}\right)^{(g+h)-(a+b)} \frac{p^g_G \cdot p^h_H}{p^a_A \cdot p^b_B} = (RT)^{(a+b)-(g+h)} K_p. \tag{5}$$

Letting Δn equal the change in the number of mols during the reaction, i.e., $(g + h) - (a + b)$

$$K_c = K_p(RT)^{-\Delta n} \tag{6}$$

In reactions where the same number of mols of gas occur on both sides of the equation, $\Delta n = 0$ and $K_c = K_p$. Since concentrations are expressed in mols per liter and partial pressures in atmospheres, it is evident that the gas constant R must be expressed in liter-atmospheres. The calculation of equilibrium constants and the relation between K_p and K_c are illustrated with the following example:

$$N_2 + 3\ H_2 = 2\ NH_3$$

$$K_c = \frac{c^2_{NH_3}}{c_{N_2} \cdot c^3_{H_2}}.$$

At 400° C. K_c has a value of 0.507 as determined by experiment and Δn is -2 at all temperatures.

$$K_p = (RT)^{\Delta n} K_c = (0.082 \times 673)^{-2}\, 0.507 = 1.66 \times 10^{-4}$$

A large value of K_p means that the numerator is greater than the denominator, and a small value means that it is smaller. In this reaction the ammonia concentration at equilibrium is high when K_p is large, and it is low when K_p is small. The magnitude of the equilibrium constant is a measure of the extent to which the reactants react to give the products — i.e., a measure of chemical affinity.

Certain conventions are observed in the use of equilibrium constants

to avoid confusion. The equation for the reaction is written down and *the products at the right of the equality sign are placed in the numerator.*

When the equation for the reaction is reversed, the new equilibrium constant becomes the reciprocal of the other. For example,

$$2\ NH_3 = N_2 + 3\ H_2$$

$$K_c = \frac{c_{N_2} \cdot c^3_{H_2}}{c^2_{NH_3}} = \frac{1}{0.507} = 1.97.$$

If the reaction is written

$$NH_3 = \tfrac{1}{2}\ N_2 + \tfrac{3}{2}\ H_2$$

$$K_c = \frac{\sqrt{c_{N_2}}\sqrt{c^3_{H_2}}}{c_{NH_3}} = \sqrt{1.97} = 1.40.$$

These fractional exponents are usually avoided through multiplication by an appropriate integer.

Free Energy Changes in Chemical Reactions. A very important relation exists between the equilibrium constant and the change in free energy. The equation has sometimes been called the *reaction isotherm*, because it applies to conditions of constant temperature.

A general reaction between perfect gases may be written as before

$$aA + bB + \ldots \rightleftarrows gG + hH + \ldots$$

and at equilibrium the partial pressures are p_A, p_B, p_G and p_H. The reaction is imagined as occurring in a special equilibrium box shown in Fig. 88. Chambers containing the gases are connected with the box through hypothetical semi-permeable membranes, each of which is permeable to only the one gas.

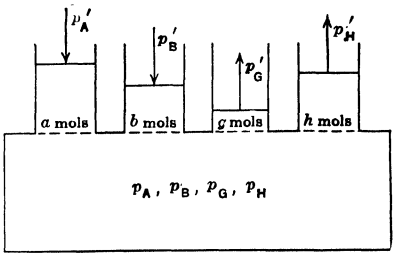


FIG. 88

The different gases in the separate chambers may have any pressures represented by p'_A, p'_B, p'_G, and p'_H.

The object of the following hypothetical operation is to determine how large a free energy change is involved in forcing the reacting materials into the box and forcing the products out.

In the first chamber a mols of the gas A are compressed* reversibly from pressure p'_A to pressure p_A, corresponding to the partial pressure

* It may be imagined that during this operation the semi-permeable membrane is covered up.

of A in the equilibrium box. The increase in free energy ΔF_1 in this operation is given by equation (7).*

$$\Delta F_1 = aRT \ln \frac{p_A}{p'_A}. \tag{7}$$

The a mols of A at pressure p_A are then forced through the semi-permeable membrane into the equilibrium box by applying a pressure infinitesimally greater than p_A. Work of compression is done in this operation, but there is no free energy change because it will be remembered that free energy change at *constant pressure* is defined as the maximum work minus the pressure-volume work, i.e. zero in this case.

In the same way b mols of B are compressed reversibly from pressure p'_B to pressure p_B and forced through the second semi-permeable membrane into the equilibrium box, and the free energy change ΔF_2 is given by equation (8),

$$\Delta F_2 = bRT \ln \frac{p_B}{p'_B}. \tag{8}$$

While a mols of A and b mols of B are being forced into the equilibrium box, g mols of G are removed by applying a pressure above the semi-permeable membrane infinitesimally less than p_G; and h mols of H are removed at pressure p_H. In this way, equilibrium conditions are maintained at all times. When these gases are removed, they are then expanded or compressed to pressures p'_G and p'_H, respectively, the free energy changes being given by

$$\Delta F_3 = gRT \ln \frac{p'_G}{p_G} \tag{9}$$

and

$$\Delta F_4 = hRT \ln \frac{p'_H}{p_H}. \tag{10}$$

The total change in free energy is

$$\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 + \Delta F_4 = aRT \ln \frac{p_A}{p'_A} + bRT \ln \frac{p_B}{p'_B} + gRT \ln \frac{p'_G}{p_G} + hRT \ln \frac{p'_H}{p_H}. \tag{11}$$

$$\Delta F = RT \ln \left(\frac{p^a_A}{p'^a_A} \frac{p^b_B}{p'^b_B} \frac{p'^g_G}{p^g_G} \frac{p'^h_H}{p^h_H} \right) \tag{12}$$

$$\Delta F = RT \ln \frac{p^a_A \cdot p^b_B}{p^g_G \cdot p^h_H} - RT \ln \frac{p'^a_A \cdot p'^b_B}{p'^g_G \cdot p'^h_H} \tag{13}$$

* Pp. 122 and 132.

$$\Delta F = -RT \ln \frac{p^{g}_{G} \cdot p^{h}_{H}}{p^{a}_{A} \cdot p^{b}_{B}} + RT \ln \frac{p'^{g}_{G} \cdot p'^{h}_{H}}{p'^{a}_{A} \cdot p'^{b}_{B}} = -RT \ln K_p + RT \ln \frac{p'^{g}_{G} \cdot p'^{h}_{H}}{p'^{a}_{A} \cdot p'^{b}_{B}}. \quad (14)$$

Now if the pressures p'_A, p'_B, p'_G, and p'_H are all 1 atmosphere the last term drops out, since $\ln 1 = 0$, and

$$-\Delta F^0 = RT \ln K_p. \quad (15)$$

The superscript zero indicates that the change in free energy corresponds to the reaction in which the reactants in their standard states, namely, at 1 atmosphere, are converted into products at 1 atmosphere.

This is an exceedingly important equation, and it will be applied to many practical problems in later chapters. It shows that the free energy decrease during a reaction is a measure of the magnitude of the equilibrium constant, i.e., of the chemical affinities involved.

This derivation may be considered as a thermodynamical proof of the validity of the equilibrium constant since the value of $-\Delta F^0$ is fixed for any reaction at constant pressure and since any partial pressures may be used in the equilibrium box, provided only that equilibrium exists. The ratio of the partial pressures is a constant then at equilibrium. A kinetic proof was given before (p. 269).

The formula

$$-\Delta F^0 = RT \ln K_c \quad (16)$$

can be derived for ideal solutions by using concentrations in mols per 1000 grams of solvent. The superscript zero indicates that the increase in free energy corresponds to the reaction in which the reactants at a concentration of 1 molal are converted into products at a concentration of 1 molal. The various solutes are transferred through hypothetical membranes which are permeable to one solute only. If a solute is volatile it can be transferred through the air.

Activities and Fugacities. Formula (16) holds strictly only for perfect gases and ideal solutions, where it can be assumed that $pv = RT$.

The equilibrium constant and its relation to free energy change are so useful that the above formulas are used even when the gases and solutions are not ideal. It is recognized that they are only approximately correct but they are often sufficiently exact for practical purposes.

To make possible exact calculations, G. N. Lewis introduced the terms *fugacity* and *activity*, which are defined in such a way that the equilibrium constant is a true constant. Fugacity has the dimensions

of pressure; it is a corrected pressure which the real gas would have if it could be converted into a perfect gas. Instead of writing that $-\Delta F^0$ is approximately equal to $RT \ln \frac{p^g_G \cdot p^h_H}{p^a_A \cdot p^b_B}$, and that the ratio $\frac{p^g_G \cdot p^h_H}{p^a_A \cdot p^b_B}$ is nearly constant, one can state that equation (17), in which fugacities f are used, is exactly true at all pressures.

$$-\Delta F^0 = RT \ln \frac{f^g_G \cdot f^h_H}{f^a_A \cdot f^b_B}. \tag{17}$$

Methods for calculating fugacities from pressures will be discussed in Chapter XIX.

Activities have the dimensions of concentrations and are in fact "effective" concentrations. If the particles of a solute exert a mutual attraction on each other, or if they combine with the solvent, or if the solvent is changed in any way so as to change the behavior of the solute, the concentrations will no longer give the same value of K over a wide range. In other words, the mass law will no longer apply. Furthermore, $-\Delta F$ will not be equal to $RT \ln K$ because the osmotic work cannot be set equal to RT. In this case the activity a is defined so that the relation must hold, and equation (18) is exact.

$$-\Delta F^0 = RT \ln \frac{a^g_G \cdot a^h_H}{a^a_A \cdot a^b_B}. \tag{18}$$

The activities may be determined, as will be explained in Chap. XIX, by referring to some standard state, i.e., to a pressure of 1 atmosphere in the case of an ideal gas, or to the condition of infinite dilution in the case of a solute.

In summarizing, it may be said that the original statement of the mass law using "active masses" is correct but that the mass law does not hold strictly with ordinary substances when concentrations or pressures are used. In order to use the mass law with precision, corrected terms, called activities and fugacities, have been invented, and they must be determined by experiment. Activities may be visualized as *effective* concentrations involving the behavior of both solute and solvent. It is sometimes stated that the mass law is exact but that the "law of concentration effect" is only approximate.

In the present chapter pressures and concentrations will be used, it being understood that the results are not exact. If the pressure is not much greater than 1 atmosphere, nor the concentration greater than 1 molal, in the case of non-electrolytes, the mass law may be assumed to hold within a few per cent. In the case of electrolytes, marked deviations are found even at concentrations much lower than 1 molal.

The calculation and use of equilibrium constants are illustrated in the following section.

Equilibrium in Homogeneous Gaseous Systems.

(a) *Dissociation of Hydriodic Acid.* A typical example of equilibrium in a gaseous system is afforded by the decomposition of hydriodic acid, as represented by the equation,

$$2\,HI \rightleftarrows H_2 + I_2.$$

This reaction has been thoroughly investigated by Hautefeuille Lemoine and Bodenstein.* The reaction is well adapted for investigation, since it proceeds very slowly at ordinary temperatures, while at the temperature of boiling sulphur, 448° C., equilibrium is established quite rapidly. If the mixture of gases is maintained at 448° C. for some time, and is then cooled quickly, the respective concentrations of the components of the mixture can be determined by the ordinary methods of chemical analysis. Various mixtures of the gases are sealed in glass tubes, and heated for a definite time in the vapor of boiling sulphur. The tubes are then cooled rapidly to the temperature of the room, and after the iodine and hydriodic acid have been removed by absorption in potassium hydroxide, the amount of free hydrogen present in each tube is measured.

Applying the law of mass action to the above equation, we have

$$\frac{c_{H_2} \cdot c_{I_2}}{c^2_{HI}} = K_c.$$

Expressing the analytical results in mols, let a mols of iodine be mixed with b mols of hydrogen, and let $2x$ mols of hydriodic acid be formed. Then, when equilibrium is established, $a - x$ will be the amount of iodine vapor, and $b - x$ will be the amount of hydrogen present. Since the concentrations are directly proportional to the amounts present, we may substitute these values for c_{H_2}, c_{I_2}, and c_{HI} in the mass-action equation. The following expression is thus obtained:

$$\frac{(b - x)(a - x)}{4x^2} = K_c. \tag{19}$$

Solving the equation for x, we obtain,

$$2x = \frac{a + b - \sqrt{a^2 + b^2 - ab(2 - 16\,K_c)}}{1 - 4\,K_c}. \tag{20}$$

Since, according to Avogadro's hypothesis, equal volumes of all gases contain the same number of molecules, volumes may be substituted for a, b, and x. Bodenstein expressed his results in terms of volumes,

* Z. Physik. Chem., **22**, 1 (1897); **29**, 295, (1899).

reduced to standard conditions of temperature and pressure. On analyzing equilibrium mixtures, Bodenstein found, that at 448° C., $K_c = 0.01984$, and at 350° C., $K_c = 0.01494$. Having determined the value of the equilibrium constant, he made use of this value to calculate the volume of hydriodic acid which should be obtained from known volumes of hydrogen and iodine. A comparison of the calculated and observed values showed excellent agreement. The following table contains a few of the results obtained by Bodenstein at 448° C.

EQUILIBRIUM IN REACTION BETWEEN HYDROGEN AND IODINE

Hydrogen, b	Iodine, a	HI calculated, $2x$	HI observed, $2x$
20.57	5.22	10.19	10.22
20.60	14.45	25.54	25.72
15.75	11.90	20.65	20.70
14.47	38.93	y	27.64
8.10	2.94	5.64	5.66
8.07	9.27	13.47	13.34

It is of interest to note that a change in pressure does not alter the equilibrium in this gaseous system. Making use of the partial pressures of the components of the gaseous system, instead of the concentrations, we have

$$\frac{p_{H_2} \cdot p_{I_2}}{p^2_{HI}} = K_p.$$

Now let the total pressure on the system be increased to n times its original value; under these conditions the partial pressures are all increased in the same proportion, and we have

$$\frac{np_{H_2} \cdot np_{I_2}}{n^2 p^2_{HI}} = K_p,$$

which will be seen to be equivalent to the original expression, since n cancels out. The equilibrium is thus seen to be independent of the pressure. This is only true for those systems in which a change in volume does not occur.

(b) *Dissociation of Nitrogen Tetroxide.* This reaction is represented by the equation

$$N_2O_4 \rightleftarrows 2\,NO_2$$

and

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}.$$

If α represents the degree of dissociation, $(1 - \alpha)$ is proportional to the number of mols of undissociated N_2O_4; 2α is proportional to the number of mols of NO_2; and $(1 - \alpha) + 2\alpha$ or $1 + \alpha$ is proportional to the total pressure.

If the total pressure is P, the partial pressures are as follows:

$$p_{N_2O_4} = \frac{1 - \alpha}{1 + \alpha} P \quad \text{and} \quad p_{NO_2} = \frac{2\alpha}{1 + \alpha} P.$$

Then

$$K_p = \frac{\left(\frac{2\alpha}{1 + \alpha} P\right)^2}{\frac{1 - \alpha}{1 + \alpha} P} = \frac{4\alpha^2 P}{1 - \alpha^2}. \tag{21}$$

At 25.0° C. and 1 atmosphere, nitrogen tetroxide has been found by vapor density measurements (p. 21) to be 18.45 per cent dissociated,

hence $$K_p = \frac{4\alpha^2 P}{1 - \alpha^2} = \frac{4 \times (0.1845)^2}{1 - (0.1845)^2} \times 1 = 0.141.$$

Having found the equilibrium constant, the degree of dissociation, α, may be found at other pressures — for example, at one-half an atmosphere,

$$K_p = 0.141 = \frac{4\alpha^2 (0.5)}{1 - \alpha^2}$$

and

$$0.141 (1 - \alpha^2) = 2\alpha^2$$

$$\alpha = 0.256.$$

In this reaction there is an increase in volume, 1 mol of gas dissociating into 2. According to the principle of Le Chatelier, it is possible to predict qualitatively that an increase of pressure will cause the system to shift toward N_2O_4, which occupies the smaller volume. Equation (21) makes it possible to calculate quantitatively the relative amounts of N_2O_4 and NO_2 at any pressure.

(c) *Dissociation of Phosphorus Pentachloride.* When phosphorus pentachloride is vaporized it dissociates according to the following equation,

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

Applying the law of mass action, we have

$$\frac{c_{PCl_3} \cdot c_{Cl_2}}{c_{PCl_5}} = K_c.$$

Starting with 1 mol of phosphorus pentachloride, which if undissociated would occupy the volume V', under atmospheric pressure, and

letting α denote the degree of dissociation, the molecular concentrations at equilibrium will be as follows:

$$c_{PCl_5} = \frac{1 - \alpha}{(1 + \alpha)\, V'}, \quad c_{PCl_3} = \frac{\alpha}{(1 + \alpha)\, V'}, \quad \text{and} \quad c_{Cl_2} = \frac{\alpha}{(1 + \alpha)\, V'}.$$

Letting $(1 + \alpha)\, V' = V$, and substituting in the above equation, we have

$$\frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1 - \alpha}{V}} = \frac{\alpha^2}{(1 - \alpha)\, V} = K_c. \tag{22}$$

At 250° C., phosphorus pentachloride is dissociated to the extent of 80 per cent. Under atmospheric pressure, 1 mol will be present in $22.4 \frac{273 + 250}{273}$ liters $= V'$. Therefore, the final volume will be,

$$V = (1 + 0.8)\left(22.4 \frac{273 + 250}{273}\right).$$

The value of the equilibrium constant — usually designated in cases of dissociation, the *dissociation constant* — is, therefore,

$$K_c = \frac{(0.8)^2}{(1 - 0.8)\,(1 + 0.8)\left(22.4 \frac{273 + 250}{273}\right)} = 0.0414.$$

The value of K_c having been obtained, the direction and extent of the reaction at 250° C. can be determined if the initial concentrations are known.

Expressing the dissociation constant in partial pressures

$$K_p = \frac{p_{PCl_3} \cdot p_{Cl_2}}{p_{PCl_5}} = K_c\,(RT)^{\Delta n} = 0.0414 \times 0.0821 \times 523 = 1.78$$

This reaction is an interesting one to study in more detail. Qualitatively, it can be seen that increasing the total pressure will decrease the amount of dissociation because the undissociated gas occupies the smaller volume. If chlorine is added, p_{Cl_2} increases and since K_p remains constant, p_{PCl_3} must diminish and p_{PCl_5} must increase. The degree of dissociation is decreased also by the addition of p_{PCl_3}. *In general the dissociation of any substance is repressed by the addition of any of the dissociation products.*

(d) *Dissociation of Carbon Dioxide.* Carbon dioxide dissociates according to the equation,

$$2\,CO_2 \rightleftarrows 2\,CO + O_2.$$

This is a somewhat more complex gaseous system than the foregoing systems. When equilibrium is established, let p_1 be the partial pressure of the carbon dioxide, p_2 the partial pressure of carbon monoxide, and p_3 the partial pressure of oxygen, then we have

$$\frac{p_2^2 \cdot p_3}{p_1^2} = K_p.$$

At 3000° C., and under atmospheric pressure, carbon dioxide is 40 per cent dissociated. The partial pressures of each of the components may be readily calculated as follows:

$$p_1 = \frac{2\,(1 - 0.40)}{2\,(1 - 0.40) + 3 \times 0.40} = 0.50,$$

$$p_2 = \frac{2 \times 0.40}{2\,(1 - 0.40) + 3 \times 0.40} = 0.33,$$

$$p_3 = \frac{0.40}{2\,(1 - 0.40) + 3 \times 0.40} = 0.17.$$

Substituting these values in the above equation, we obtain,

$$K_p = \frac{(0.33)^2 \times 0.17}{(0.50)^2} = 0.074.$$

Equilibrium in Liquid Systems. The reaction between an alcohol and an acid, to form an ester and water, may be taken as an example of equilibrium in a liquid system. In the reaction,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

let a, b, and c represent the number of mols of alcohol, acid and water, respectively, which were initially present in V liters of the mixture, and let x denote the number of mols of ester and water which have been formed, when the system has reached equilibrium.

The concentrations of the components will be,

$$c_{\text{alc.}} = \frac{a - x}{V}, \quad c_{\text{acid}} = \frac{b - x}{V}; \quad c_{\text{ester}} = \frac{x}{V}; \quad \text{and} \quad c_{\text{water}} = \frac{c + x}{V}.$$

Applying the law of mass action, we obtain,

$$K_c = \frac{c_{\text{ester}} c_{\text{water}}}{c_{\text{alc.}} c_{\text{acid}}} = \frac{x(c + x)}{(a - x)\,(b - x)} \tag{23}$$

This reaction has been studied, as already mentioned, by Berthelot and Péan de St. Gilles. They found that when equivalent amounts of alcohol and acid are mixed, the reaction proceeds until two-thirds of the mixture is changed into ester and water. Hence, we find,

$$K_c = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4. \tag{24}$$

Having determined the value of K_c, it may now be used to calculate the equilibrium conditions for any initial concentrations of the substances involved in the reaction. As an illustration, we will take 1 mol of acetic acid and treat it with varying amounts of alcohol, the initial mixture containing neither of the products of the reaction. The equation takes the form,

$$\frac{x^2}{(a - x)(1 - x)} = 4.$$

Solving for x, we have,

$$x = \tfrac{2}{3}(1 + a - \sqrt{a^2 - a + 1}). \qquad (25)$$

A comparison of the observed and calculated values, given in the accompanying table, shows that the agreement is excellent, even in the more concentrated solutions where we might reasonably expect that the law of concentration effect would cease to hold.

EQUILIBRIUM IN THE REACTION BETWEEN ACETIC ACID AND ALCOHOL

Alcohol, a	Ester (observed), x	Ester (calculated), x
0.05	0.05	0 049
0.08	0.078	0 078
0.18	0.171	0.171
0.28	0.226	0 232
0.33	0.293	0.311
0.50	0.414	0.423
0.67	0.519	0.528
1.0	0.665	0.667
1.5	0.819	z
2.0	0 858	0.845
2.24	0.876	0.864
8.0	0.966	0.945

In the equilibrium just studied the volume terms, V, cancel out, and the equilibrium constant is not affected by changing the volume. The volume terms do not cancel out when there is a change in the number of molecules and the equilibrium concentrations are changed by diluting the mixture.

In solutions as concentrated as the ones just studied the equilibrium constants are often unsatisfactory unless activities are used in place of concentrations. Some solutions are sufficiently near to ideal solu-

tions so that fairly reliable constants can sometimes be obtained even with concentrations. Better results are obtained in concentrated solutions by using molal concentrations rather than molar concentrations, because in molal solutions the volume of the solute is not included. It will be remembered that the gas laws hold better when the volume of the molecules is subtracted from the total volume. Mol fractions sometimes give more satisfactory constants than concentrations in concentrated solutions.

Influence of Temperature on Chemical Equilibrium. According to equation (15)

$$-\Delta F^0 = RT \ln K_p \tag{26}$$

Differentiating*

$$d(-\Delta F^0) = R\,dT \ln K_p + RT\,d \ln K_p. \tag{27}$$

According to the Gibbs-Helmholtz equation

$$\Delta H - \Delta F^0 = T\frac{d(-\Delta F^0)}{dT}. \tag{28}$$

Substituting in (28) the value of $d(-\Delta F^0)$ obtained in (27),

$$\Delta H - \Delta F^0 = T\frac{R \ln K_p\,dT + RT\,d \ln K_p}{dT}, \tag{29}$$

and

$$\Delta H - \Delta F^0 = RT \ln K_p + RT^2\frac{d \ln K_p}{dT}. \tag{30}$$

Subtracting equation (15) from equation (30) and rearranging,

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}. \tag{31}$$

This is a very important equation which is used for calculating heats of reaction from chemical equilibria, and for calculating equilibrium constants at different temperatures. The Clapeyron equation, already discussed, is a special case of this more general equation. In fact, the equilibrium constant K_p can be extended to include any type of equilibrium such as reactions of gases, or solutes, vaporization of liquids, and sublimation or solubility of solids.

Over small temperature ranges ΔH can be assumed to be constant, and integration of equation (31) gives

$$\ln K_p = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + C. \tag{32}$$

Data are given in the following table for the dissociation of nitrogen

* The differentiation of a product is given by the rule $d(uv) = u\,dv + v\,du$.

tetroxide; in Fig. 89, values of log K_p for the dissociation of nitrogen tetroxide are plotted against $1/T$, and it is evident that a straight line is produced. Such a result is to be expected from equation (32) and,

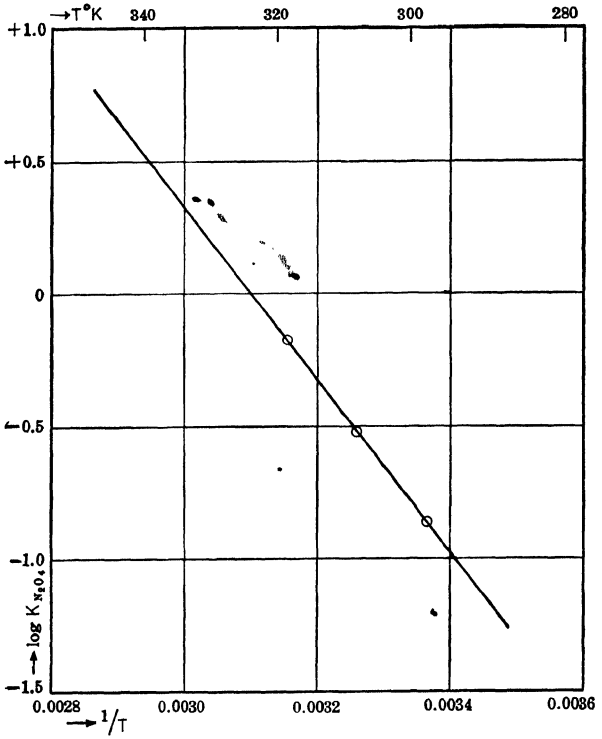


FIG. 89

in fact, the heat of dissociation, ΔH, can be calculated from the slope of the line, as follows:

$$-\Delta H = \text{slope} \times 2.303\, R. \tag{33}$$

In the case of nitrogen tetroxide ΔH is 14,600 since the slope is −3188.7, and R is 1.987 calories.

The value of the integration constant C in equation (32) can be determined from experimental values of K_p at definite temperatures, and the practical working equation becomes

$$\log K_p = \frac{-14{,}600}{4.576T} + 9.8500.$$

It is evident that K_p becomes larger as the temperature increases, i.e., the dissociation becomes greater. Also, according to equation

DISSOCIATION CONSTANTS OF N_2O_4

T	K	$1/T$	$\log K$
288°	0.060	0.003472	−1.222
298	0.141	0.003356	−0.850
308	0.315	0.003247	−0.502
318	0.664	0.003145	−0.178
328	1.349	0.003048	+0.130
338	2.607	0.002958	+0.416
348	4.867	0.002873	+0.687

(15) the decrease in free energy becomes greater, indicating greater dissociation. Equation (31) can be solved also by integrating between limits K_{p_2} at T_2 and K_{p_1} at the lower temperature T_1, as was done on p. 130.

$$\ln K_{p_2} - \ln K_{p_1} = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{34}$$

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303\,R}\left(\frac{T_2 - T_1}{T_2 \times T_1}\right). \tag{35}$$

Substituting the data for N_2O_4 at 298° and 338° into equation (35),

$$\log \frac{K_{p_2}}{K_{p_1}} = \log \frac{2.607}{0.141} = \frac{\Delta H}{2.303 \times 1.988}\left(\frac{338 - 298}{338 \times 298}\right),$$

and

$$\Delta H = 14{,}600.$$

An expression similar to (31) can be derived for conditions of constant volume as follows:

$$K_p = K_c\,(RT)^{\Delta n},$$

$$\ln K_p = \ln K_c + \Delta n \ln RT. \tag{36}$$

Solving for K_c and differentiating

$$\frac{d \ln K_c}{dT} = \frac{d \ln K_p}{dT} - \frac{d(\Delta n \ln R)}{dT} - \frac{d(\Delta n \ln T)}{dT}. \tag{37}$$

Since the derivative of the constant term $\Delta n \ln R$ is zero,

$$\frac{d \ln K_c}{dT} = \frac{\Delta H}{RT^2} - \frac{\Delta n}{T} = \frac{\Delta H - \Delta nRT}{RT^2}. \tag{38}$$

But

$$\Delta H = \Delta U + p\Delta v,$$

and according to the gas law, $p\Delta v$ is the work done by the expanding gases, i.e. ΔnRT. Therefore

$$\Delta U = \Delta H - \Delta nRT$$

and equation (38) becomes

$$\frac{d \ln K_c}{dT} = \frac{\Delta U}{RT^2}. \tag{39}$$

ΔH represents the heat absorbed at constant pressure, q_p; and ΔU represents the heat absorbed at constant volume, q_v. Equation (39) was first derived by van't Hoff; it is known as van't Hoff's *reaction isochore* because it is used under conditions of constant volume.

If there is no change in the volume of the system $\Delta n = 0$, $K_c = K_p$, and $\Delta H = \Delta U$. Reactions in solution where no gas is evolved are examples of this class.

In a reaction which is accompanied by no thermal change, $\Delta U = \Delta H = 0$, and the right-hand side of equations (31) and (39) becomes equal to zero. In other words, in such a reaction a change in temperature does not cause a displacement of the equilibrium.

The reaction,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COO.C_2H_5 + H_2O,$$

is accompanied by such a small thermal change that it may be considered as zero, and according to the above reasoning, there should be only a very slight displacement of the equilibrium when the temperature is varied. Berthelot found that at 10° C., 65.2 per cent of the alcohol and acid are changed into ester, and at 220° C., 66.5 per cent of the mixture is transformed into ester. As will be seen, an increase of 210° produces hardly any displacement of the equilibrium.

REFERENCES

Treatise on Physical Chemistry. Taylor. Chapter VIII.
Thermodynamics and the Free Energy of Chemical Substances. Lewis and Randall. Chapter XXIV.
Chemical Statics and Dynamics. Mellor.
A System of Physical Chemistry. Lewis, Vol. II. Chapters V and XII.

PROBLEMS

1. Calculate the value of y in the table on page 276.

2. When 2.94 mols of iodine and 8.10 mols of hydrogen are heated at constant volume at 444° C. until equilibrium is established, 5.64 mols of hydriodic acid are formed. If we start with 5.30 mols of iodine and 7.94 mols of hydrogen, how much hydriodic acid is present at equilibrium at the same temperature?

Ans. 9.49 mols.

3. For the dissociation of hydriodic acid at 350°, $K_c = 0.01494$. (*a*) How many mols of hydriodic acid will be formed when 10 g. of iodine and 0.05 g. of hydrogen are heated to 350° in a 1-liter vessel? (*b*) What will be the partial pressures of hydriodic acid and each of the dissociation products?

4. At 35°, N_2O_4 is dissociated to the extent of 27 per cent, under a pressure of 1 atmosphere. Calculate K_p and K_c.

5. At 35°, N_2O_4 is dissociated to the extent of 27 per cent under a pressure of 1 atmosphere. (*a*) Calculate the extent of dissociation at a pressure of 100 mm. (*b*) What total pressure is necessary to give a partial pressure of NO_2 amounting to 100 mm.?

6. The following equation has been found to apply to the reaction $N_2O_4 \rightleftarrows 2\ NO_2$:

$$\log K_p = -\frac{14{,}600}{4.576T} + 9.8500.$$

(*a*) Calculate the value of K_p at 50°. (*b*) Calculate the degree of dissociation at this temperature when the total pressure is 1 atmosphere.

7. One-tenth of a mol of phosphorus pentachloride is heated to 250° in a 2-liter vessel. At this temperature the dissociation proceeds according to the reaction $PCl_5 \rightleftarrows PCl_3 + Cl_2$ and K_c has the value 0.0414. (*a*) What is the concentration of chlorine in mols per liter? (*b*) What is the partial pressure of chlorine in millimeters?

8. At 2000° C., and under atmospheric pressure, carbon dioxide is 1.80 per cent dissociated according to the equation

$$2\ CO_2 \rightleftarrows 2\ CO + O_2.$$

Calculate the equilibrium constant for the above reaction using partial pressures.

Ans. 3×10^{-6}.

9. What is the equilibrium constant in the preceding problem, if the concentrations are expressed in mols per liter?

10. For the gaseous reaction, $COCl_2 \rightleftarrows CO + Cl_2$, at 100° the dissociation constant, K_p, is 6.7×10^{-9}. Calculate the partial pressure of carbon monoxide in equilibrium with phosgene at this temperature under a total pressure of 1 atmosphere. The dissociation is so slight that the partial pressure of phosgene may be taken as equal to the total pressure.

11. The equilibrium constant, K_p, for the reaction, $\frac{1}{2}\ N_2 + \frac{3}{2}\ H_2 \rightleftarrows NH_3$, at 437° C. is 0.0078 (at 50 atmospheres). Starting with a mixture of gas containing three parts of hydrogen to one part of nitrogen calculate the partial pressure of ammonia at equilibrium when the total pressure on the gas mixture is 50 atmospheres. It will be remembered that the total pressure is the sum of the partial pressures of the three substances and that the partial pressure of hydrogen is always three times the partial pressure of nitrogen irrespective of the amount of ammonia formed.

Ans. 5 atmos.

12. The reaction, $CO_2 + H_2 \rightleftarrows CO + H_2O$, was investigated by passing mixtures of carbon dioxide and hydrogen over a catalyst at a high temperature. The resulting gas was chilled quickly to room temperature by passage through a capillary, and analyzed. In one experiment the partial pressures were as follows: CO_2 0.2122; H_2 0.2295; CO 0.2792; H_2O 0.2792 atmos. (*a*) Calculate the value of the equilibrium constant K_p. (*b*) Calculate the number of mols of hydrogen present in an equilibrium mixture containing 22.82 mols of carbon monoxide, 22.82 mols of water and 47.50 mols of carbon dioxide. (*c*) What is the composition of the initial mixture of carbon dioxide and hydrogen which will give the equilibrium composition described in (*b*)?

13. When sulphur dioxide is oxidized to sulphur trioxide in the presence of a catalyst at 727° C. the following relation holds:

$$K_p = 1.85 = \left(\frac{p_{SO_3}}{p_{SO_2}}\right) \frac{1}{\sqrt{p_{O_2}}}$$

(*a*) What is the ratio of SO_3 to SO_2 when the partial pressure of oxygen at equilibrium is 0.2 atmosphere?

(*b*) What is the ratio of SO_3 to SO_2 when the partial pressure of oxygen is 0.5 atmosphere?

(*c*) What is the effect on the ratio SO_3/SO_2 when the equilibrium mixture described in (*a*) is compressed so that the total pressure is doubled?

(*d*) What is the effect on the ratio SO_3/SO_2 if the total pressure of the mixture of gases is increased by forcing in nitrogen under pressure?

14. Calculate the value of z in the table on page 280.

15. If 1 mol of acetic acid and 1 mol of ethyl alcohol are mixed, the reaction

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

proceeds until equilibrium is reached, when $\frac{1}{3}$ mol of ethyl alcohol, $\frac{1}{3}$ mol of acetic acid, $\frac{2}{3}$ mol of ethyl acetate, and $\frac{2}{3}$ mol of water are present. If we start (*a*) with 1 mol of acid and 2 mols of alcohol; (*b*) with 1 mol of acid, 1 mol of alcohol, and 1 mol of water; (*c*) with 1 mol of ester and 3 mols of water, how much ester will be present in each case at equilibrium?

16. When 0.00663 mol of amylene and 0.001 mol of acetic are mixed in 894 cc. of an inert solvent, 0.000838 mol of ester is formed according to the reaction

$$CH_3COOH + C_5H_{10} \rightleftarrows CH_3COOC_5H_{11}.$$

How much ester will be formed when one mixes 0.00448 mol of amylene and 0.001 mol of acetic acid in 683 cc. *Ans.* 0.000811 mol.

17. Adkins and Adams studied the equilibria involved in the formation of acetals by titrating the mixture and determining the aldehyde concentration. At 25° 1 mol of ethanol was mixed with 0.091 mol of acetaldehyde in a volume of 63.0 cc. and it was found that when equilibrium was reached, 90.72 per cent of the acetaldehyde had reacted. The reaction is:

$$2\,C_2H_5OH + CH_3CHO = CH_3CH(OC_2H_5)_2 + H_2O.$$

Calculate the equilibrium constant, assuming an ideal solution.

18. Sulphur trioxide dissociates according to the reaction $SO_3 \rightleftarrows SO_2 + \frac{1}{2}\,O_2$ and the values of K_p are as follows:

Temp. (C)	528°	627°	727°	832°
K_p	0.0319	0.153	0.540	1.59

Plot log K_p against $1/T$ and determine the heat of dissociation from the slope of the line.

19. The dissociation constant, K_p, for sulphur trioxide is 0.0319 at 528° and 0.540 at 727° C. (*a*) Calculate ΔH for the dissociation. (*b*) Calculate the value of K_p at 600° C.

20. Above 150° C. NO_2 dissociates according to the equation $NO_2 \rightleftarrows NO + \frac{1}{2}\,O_2$. At 390° C. and 1 atmosphere pressure the partially dissociated gas is 19.57 times as heavy as hydrogen, and at 490° C. it is 18.04 times as heavy. (*a*) What is the degree of dissociation at these two temperatures? (*b*) What are the dissociation constants at the two temperatures? (*c*) What is the heat of dissociation?

Ans. (*a*) At 390° $\alpha = 0.332$.
(*b*) At 390° $K_p = 0.1875$.
(*c*) $\Delta H = 9407$ cal.

21. In a determination of the keto-enol equilibrium of aceto-acetic ester, the concentration of the enol form in a solution of 2.6038 g. of ester in 100 cc. alcohol was found to be 0.02085 molar at 25° and 0.0184 molar at 40°. (*a*) Calculate K_c at each temperature. (*b*) Calculate the heat evolved when one mol of the keto form is transformed into the enol form. The reaction is

$$CH_3(CO)CH_2COOC_2H_5 \rightleftarrows CH_3C(OH)=CHCOOC_2H_5.$$

CHAPTER XIII

HETEROGENEOUS EQUILIBRIUM

Heterogeneous Systems. We have now to consider equilibria in systems made up of matter in different states of aggregation. Such systems are termed *heterogeneous systems*, as distinguished from those dealt with in the preceding chapter, where the composition is uniform throughout. The physically distinct portions of matter involved in a heterogeneous system are known as *phases*, each phase being homogeneous and having uniform physical and chemical properties, and being separated from the other phases by definite bounding surfaces. Thus, ice, liquid water, and vapor constitute a physically heterogeneous system. Another heterogeneous system is formed by calcium carbonate and its products of dissociation, calcium oxide and carbon dioxide. The equilibrium between a solid, its saturated solution, and vapor affords an illustration of a still more complex heterogenous system.

Application of the Law of Mass Action to Heterogeneous Equilibria. It has been shown in the preceding chapter that the law of mass action may be applied to homogeneous equilibria, provided the molecular condition of the reacting substances is known.

When we attempt to apply the law of mass action to heterogeneous equilibria, especially where solids are involved, the problem presents difficulties. In his investigation of the dissociation of calcium carbonate, according to the equation,

$$CaCO_3\,(s) \rightleftarrows CaO\,(s) + CO_2\,(g),$$

Debray* showed, that just as every liquid has a definite vapor pressure corresponding to a certain temperature, so there is a definite pressure of carbon dioxide over calcium carbonate, at a definite temperature. Furthermore, the pressure was found to be independent of the amount of calcium carbonate present.

Guldberg and Waage† showed that the law of mass action can be applied to such heterogeneous equilibria, provided that the active masses of the solids present are considered as constant. Nernst confirmed this statement of Guldberg and Waage and showed how it can

* Compt. rend., **64**, 603 (1867).

† Loc. cit.

be reconciled with experimental facts. In a heterogeneous equilibrium involving solids, it is only necessary to consider the gaseous phase, since the active mass of a solid is equivalent to its concentration in the gaseous phase. That is, every solid is to be looked upon as possessing, at a definite temperature, a definite vapor pressure which is entirely independent of the amount of solid present. Such substances as arsenic, antimony, and cadmium are known to have appreciable vapor pressures at relatively low temperatures, and it is quite reasonable to suppose that every solid substance exerts a definite vapor pressure at a definite temperature, even though we have no method sufficiently refined to measure such minute pressures.

Since the active mass of a solid remains constant so long as any of it is present, the application of the law of mass action to certain heterogeneous equilibria is, in general, simpler than its application to homogeneous systems. The truth of this statement will be evident after a few typical heterogeneous systems have been considered.

(a) *Dissociation of Calcium Carbonate.* In the reaction,

$$CaCO_3\,(s) \rightleftarrows CaO\,(s) + CO_2\,(g),$$

let π_1 and π_2 represent the pressures due to the vapor of calcium carbonate and calcium oxide, respectively, and let p denote the pressure of the carbon dioxide. Applying the law of mass action, we obtain,

$$\frac{\pi_2 p}{\pi_1} = K_p.$$

But, since π_1 and π_2 are constant at any one temperature, the equation becomes,

$$p = K_p',$$

or, the equilibrium constant, at any one temperature, is solely dependent upon the pressure of the carbon dioxide evolved. The accompanying table gives the values of the pressure of carbon dioxide corresponding to various temperatures.

(b) *Dissociation of Ammonium Hydrosulphide.* When solid ammonium hydrosulphide is heated, it is almost completely dissociated into ammonia and hydrogen sulphide, as shown by the following equation:

$$NH_4HS\,(s) \rightleftarrows NH_3\,(g) + H_2S\,(g).$$

This reaction was investigated by Isambert,* who found that the total gas pressure at 25.1° C., is equal to 501 mm. of mercury. Since the partial pressures of the ammonia and hydrogen sulphide are necessarily

* Compt. rend., **93**, 595, 730 (1881).

DISSOCIATION PRESSURES OF $CaCO_3$

Temperature, Degrees C.	Pressure in Atmospheres
500	0.000096
600	0.00242
700	0.0292
800	0.220
897	1.000
1000	3.871
1100	11.499
1200	28.680

the same, each must be approximately equal to 250.5 mm., the relatively small pressure due to the undissociated vapor of the ammonium hydrosulphide being neglected. Let π be the partial pressure of the vapor of ammonium hydrosulphide, and let p_1 and p_2 be the partial pressures of the ammonia and hydrogen sulphide respectively. Applying the law of mass action, we have

$$\frac{p_1 \cdot p_2}{\pi} = K_p. \tag{1}$$

Since π is constant at any one temperature, equation (1) becomes,

$$p_1 \cdot p_2 = K_p'.$$

According to Dalton's law of partial pressures, we have

$$P = p_1 + p_2 + \pi,$$

where P is the total pressure. Neglecting the relatively small pressure π, we may write,

$$P = p_1 + p_2.$$

It must be clearly understood that π is neglected in determining the total pressure because it is small, but that it disappears in the new equilibrium constant K' not because it is small but because it is *constant*. Hence, since $p_1 = p_2$,

$$\frac{P}{2} = p_1 = p_2.$$

Substituting these values in equation (1), we obtain

$$\frac{P^2}{4} = K_p' = \frac{(501)^2}{4} = 62{,}750.$$

The value of the equilibrium constant may be checked, by observing the effect on the system of the addition of an excess of either one of the products of the dissociation. The accompanying table gives the results of a few of Isambert's experiments.

DISSOCIATION PRESSURES OF NH_4HS (25.1°)

Pressure of Ammonia	Pressure of Hydrogen Sulphide	$p_{NH_3} \cdot p_{H_2S} = K_p'$
208	294	61,152
138	458	63,204
417	146	60,882
453	143	64,779
		Mean 62,504

As will be seen, the mean value of the equilibrium constant agrees well with the value found for equivalent amounts of the products of dissociation.

(c) *Dissociation of Ammonium Carbamate.* The dissociation of ammonium carbamate takes place according to the equation,

$$OC\begin{matrix}ONH_4\\NH_2\end{matrix} \rightleftarrows 2\,NH_3 + CO_2.$$

This dissociation has been investigated by Horstmann.* Applying the law of mass action, we have

$$\frac{p_1^2 \cdot p_2}{\pi} = K_p, \tag{2}$$

where p_1 and p_2 are the partial pressures of ammonia and carbon dioxide respectively, and where π is the partial pressure of ammonium carbamate. Since π is constant in the presence of the solid, equation (2) becomes

$$p_1^2 \cdot p_2 = K_p'. \tag{3}$$

If P denotes the total gaseous pressure, and π is neglected as in the preceding example, we have, since 3 mols of gas are formed,

$$p_1^2 = \frac{4\,P^2}{9} \quad \text{and} \quad p_2 = \frac{P}{3}.$$

* Lieb. Ann., **187**, 48 (1877).

Substituting these values in equation (3), we have

$$\frac{4\,P^3}{27} = K_p'. \tag{4}$$

This equation has also been tested by Isambert,* by adding an excess of ammonia, or carbon dioxide, to the dissociating system. He found that the value of the equilibrium constant remains practically constant. Furthermore, the addition of a foreign gas was shown to be without effect. Briggs and Migrdichian* studied the equilibrium with great care.

(d) *Dissociation of the Hydrates of Copper Sulphate.* Many interesting examples of heterogeneous equilibrium are furnished by hydrated salts. Thus, if crystallized copper sulphate, $CuSO_4 \cdot 5\,H_2O$, is placed in a desiccator, it gradually loses water of crystallization, and ulti-

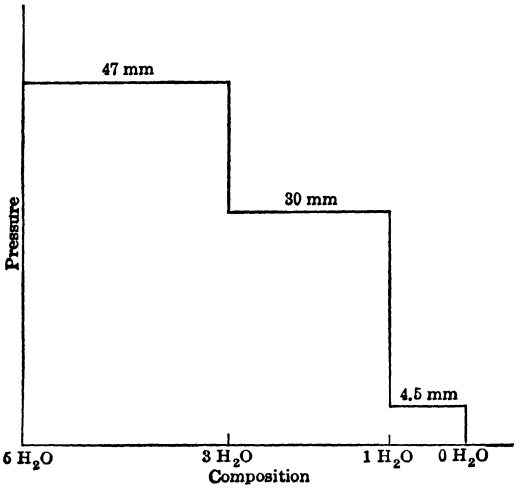


FIG. 90

mately the anhydrous salt alone remains. If a desiccator, provided with a manometer, is placed in a thermostat, it is possible to observe the changes in vapor pressure accompanying the process of dehydration. At the temperature of 50° C., the pressure over completely hydrated copper sulphate is found to remain constant at 47 mm., until the salt has been deprived of 2 molecules of water, when it drops abruptly to 30 mm., and remains constant until 2 more molecules of water have been lost. It then drops to 4.5 mm., and remains constant until dehydration is complete.

The successive stages of the dehydration are shown in the accom-

* Loc. cit. † J. Phys. Chem. 28, 1121 (1924).

panying diagram, Fig. 90. The constant pressures observed in the dehydration correspond to the successive equilibria involved. At 50° C., the pentahydrate and the trihydrate are in equilibrium, a pressure of 47 mm. being maintained so long as any of the pentahydrate is present. When all of the pentahydrate has disappeared, then the trihydrate begins to undergo dehydration into the monohydrate. This is a new equilibrium, and the pressure of the aqueous vapor necessarily changes, and remains constant so long as any trihydrate remains. The last stage corresponds to the equilibrium between the monohydrate and the anhydrous salt. The following equations represent the three successive equilibria:

(1) $CuSO_4 \cdot 5\,H_2O \rightleftarrows CuSO_4 \cdot 3\,H_2O + 2\,H_2O$,
(2) $CuSO_4 \cdot 3\,H_2O \rightleftarrows CuSO_4 \cdot H_2O + 2\,H_2O$,
(3) $CuSO_4 \cdot H_2O \rightleftarrows CuSO_4 + H_2O$.

Applying the law of mass action to the first of the above equilibria, we have

$$\frac{\pi_2 p^2}{\pi_1} = K_p,$$

in which π_1 and π_2 denote the partial pressures due to the hydrates, $CuSO_4 \cdot 5\,H_2O$ and $CuSO_4 \cdot 3\,H_2O$, respectively, and p denotes the pressure of aqueous vapor. Since π_1 and π_2 are constant, the above expression takes the form,

$$p^2 = K_p'.$$

In a similar manner, it may be shown that the pressure of aqueous vapor in the other equilibria must be constant. It must be clearly understood that the observed pressure is definite and fixed only when two hydrates are present.

Distribution of a Solute between Two Immiscible Solvents. When an aqueous solution of succinic acid is shaken with ether, the acid distributes itself between the ether and the water in such a way that the ratio between the two concentrations is always constant. It will be seen that the distribution of succinic acid between two solvents is analogous to that of a substance between the liquid and gaseous phases (p. 141), and therefore, the laws governing the latter equilibrium should apply equally to the former. Nernst* has shown that (a) *If the molecular weight of the solute is the same in both solvents, the ratio in which it distributes itself between them is constant, at constant temperature,* or, in other words, Henry's law is applicable; and (b) *If there are several*

* Z. physik. Chem., **8**, 110 (1891).

solutes in solution, the distribution of each solute is the same as if it were present alone. This is clearly Dalton's law of partial pressures. The ratio in which the solute distributes itself between the two solvents is termed the *coefficient of distribution.* The following table gives the results of three experiments on the distribution of succinic acid between ether and water.

DISTRIBUTION OF SUCCINIC ACID (14°)

Concentration in Water	Concentration in Ether	Distribution Coefficient
43.4	7.1	6 1
43.8	7.4	5.9
47.4	7.9	6.0

As will be seen, the distribution coefficient is constant, showing that Henry's law applies. When the molecular weight of a solute is not the same in both solvents, the distribution coefficient is not constant, and conversely, if the distribution coefficient is not constant, we infer that the molecular weights of the solute in the two solvents are not identical.

Let us assume that a solute whose normal molecular weight is A, when shaken with two immiscible solvents, undergoes polymerization in one of them, its molecular weight being A_n. We then have the equilibrium,

$$A_n \rightleftarrows nA.$$

Applying the law of mass action, we have

$$\frac{c^n_A}{c_{A_n}} = K_c. \tag{5}$$

If the molecular weight in one solvent is twice the molecular weight in the other, then $n = 2$, and

$$\frac{c_1^2}{c_2}, \quad \text{or} \quad \frac{c_1}{\sqrt{c_2}} = \text{constant.}$$

Thus, Nernst found the following concentrations of benzoic acid when it was shaken with benzene and water.

As will be seen, the values of the ratio c_1/c_2 steadily decrease, while on the other hand, the values of the ratio $c_1/\sqrt{c_2}$ remain constant. This shows, therefore, that benzoic acid has twice the normal molecular weight in benzene.

This fact is fully corroborated by direct measurements of molecular weight, the elevation of the boiling-point being only half as large as

DISTRIBUTION OF BENZOIC ACID (20°)

c_1 (Water)	c_2 (Benzene)	$\frac{c_1}{c_2}$	$\frac{c_1}{\sqrt{c_2}}$
0.0150	0.242	0.062	0.0305
0 0195	0.412	0.048	0.0304
0.0289	0.970	0.030	0.0293

expected on the assumption that the molecular weight is the sum of the atomic weights. Benzoic acid gives a normal molecular weight in alcohol and in many other solvents; and moreover benzene does not cause association or polymerization of all solutes. The phenomena are not fully understood but it seems likely that substances which give associated molecules in the gas phase (on account of special groupings in the crystal lattice, or on account of unsatisfied valencies or for other reasons) will give associated molecules also in benzene and certain inert solvents. Other solvents like water and alcohol which are themselves associated, on the other hand, appear to be able to break down the associated solute molecules.

When the solute is very sparingly soluble, the distribution ratio is identical with the ratio of solubilities in the two solvents. In most cases, however, the saturated solutions are so concentrated and so far from ideal that the mass law no longer holds. Under these conditions the coefficient of distribution changes with the concentration, and the distribution ratio in dilute solution may differ largely from the solubility ratio. The distribution ratio can be made constant at all concentrations by using activities in place of concentrations, but the activities are more difficult to determine experimentally, as will be explained in a later chapter. (Chapter XIX.)

Variation of the Constant of Heterogeneous Equilibrium with Temperature. The van't Hoff equation derived on p. 283,

$$\ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H(T_2 - T_1)}{RT_2T_1},$$

which expresses the variation of the equilibrium constant with temperature, applies equally well to heterogeneous equilibria. The following examples will serve to illustrate its application in such cases. Other examples have been given before on pp. 130 and 136.

(a) *Dissociation of Ammonium Hydrosulphide.* In the reaction representing the dissociation of ammonium hydrosulphide,

$$NH_4HS\ (s) \rightleftarrows NH_3\ (g) + H_2S\ (g),$$

let p_1 and p_2 be the partial pressures of ammonia and hydrogen phide, and let π be the partial pressure of ammonium hydrosulphide. Then, as has been shown,

$$K_p = \frac{p_1 p_2}{\pi} \quad \text{and} \quad K'_p = p_1 p_2 = \frac{P^2}{4}$$

where P is the total gaseous pressure. From the following data:

$$T_1 = 273° + 9.5°, \qquad P_1 = 175 \text{ mm. of mercury,}$$

and

$$T_2 = 273° + 25.1°, \qquad P_2 = 501 \text{ mm. of mercury,}$$

we have, on applying the reaction isochore equation, and solving for ΔH,

$$\Delta H = \frac{4.576\left[\log\left(\frac{501}{2}\right)^2 - \log\left(\frac{175}{2}\right)^2\right] 282.5 \times 298.1}{298.1 - 282.5},$$

or,

$$\Delta H = 22{,}570 \text{ cal.}$$

This result agrees well with the value, 22,800 calories, found by direct experiment.

(b) *Solution of Succinic Acid.* When a solid is introduced into a non-dissociating solvent, it continues to dissolve, until the solution becomes saturated. A condition of equilibrium then obtains, and the rates of solution and precipitation are the same. This is plainly a case of heterogeneous equilibrium. If c is the concentration of the dissolved substance, and π is the concentration in the solid state, then, according to the law of mass action,

$$\frac{c}{\pi} = K_c,$$

or, since π is constant,

$$c = K_c'.$$

The following experimental data of van't Hoff enable us to calculate the heat of solution ΔH of succinic acid in water.

$$T_1 = 273°, \quad c = 28.8 \text{ g. per } 1000 \text{ g. of water}$$

$$T_2 = 281.5°, \quad c = 42.2 \text{ g. per } 1000 \text{ g. of water}$$

$$\Delta H = \frac{4.576 \ (\log 42.2 - \log 28.8) \ 273 \times 281.5}{281.5 - 273} = 6865 \text{ cal.}$$

The heats of solution calculated in this way agree well with the experimentally observed results. It must be remembered, however, that the calculated value gives the heat of solution in a saturated solution, whereas the heats given in tables frequently apply to solutions in an

nitely dilute solution. The two values will differ by an amount equal to the heat of dilution.

The Phase Rule. When studying the behavior of heterogeneous systems in a state of equilibrium we make use of a generalization discovered by J. Willard Gibbs,* who was professsor of mathematical physics at Yale University. This generalization was first stated by Gibbs in 1874 and is commonly known as the phase rule. The phase rule together with his monumental generalizations in thermodynamics have given Gibbs a position as one of the great geniuses of science. The fundamental statement of the phase rule is simply

$$F = C - P + 2. \tag{6}$$

The number of phases P is the number of separate physical states which exist in a system at equilibrium. They may be gas, liquid, or solids of different kinds. Phases are regions which are physically and chemically uniform; they are separated from other phases by bounding surfaces.

The number of degrees of freedom, F, is the number of independent variables such as temperature, pressure and concentration which must be specified in order to describe the system completely.

The number of components C is the number of independent chemical individuals which must be specified in order to describe the chemical nature of the system.

The phase rule can be derived in a satisfactory manner, but it will be sufficient here to illustrate with specific examples its meaning and importance. It should be pointed out that the phase rule applies only to systems which are in *equilibrium*, and that it does not predict new things but is very valuable in correlating data. Phase-rule diagrams are of great help in practical problems involving many variables, such for example as the extraction of potassium chloride from the Stassfurt salt deposits.

Equilibrium in the System, Water, Ice, Vapor. This is a one-component system, water being the only chemical individual involved. It is true that water dissociates into hydrogen and oxygen at high temperatures, but this reaction may be neglected in the neighborhood of room temperature. Three phases are possible — solid, liquid, and vapor — and the number of these which can exist in equilibrium at one time depends on the conditions of temperature and pressure. These conditions have been determined by direct experimental measurement and are summarized in the pressure-temperature diagram shown in Fig. 91.

* Trans. Conn. Acad., Vols. II and III (1875–8).

The vapor-pressure curve of water is represented by the line Above this line liquid water exists alone; and below it water vapor exists alone. Only on the line *OA* where both regions touch is it possible to have both water and its vapor in equilibrium. Thus if the pressure is reduced to a point below the line *OA*, all the water will be vaporized; if, on the other hand, the pressure is raised above the curve, all the vapor will ultimately condense to the liquid state.

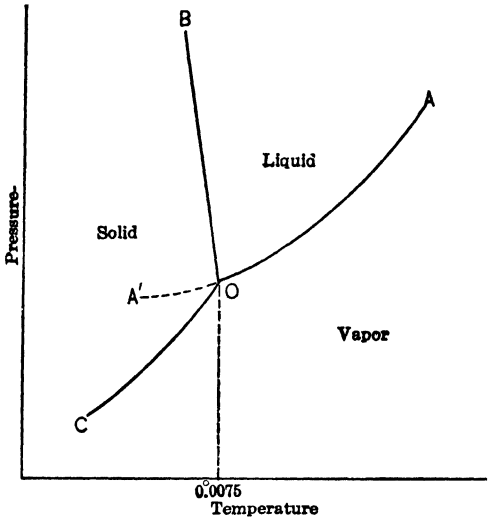


FIG. 91

The application of the phase rule may now be illustrated. Vapor may exist anywhere in the area labeled "vapor," and it is necessary to specify both the pressure and the temperature in order to define the system completely. The mere statement that water vapor is present at a specified pressure does not describe the system, because the temperature variable is not defined. There is one phase (vapor) and one component so the phase rule indicates that there are two degrees of freedom, as shown in equation (7).

$$F = C - P + 2 = 1 - 1 + 2 = 2. \qquad (7)$$

In the region labeled "liquid" there is one phase (water) and one component so that there are again two degrees of freedom.

Along the line *OA* there are two phases, water and vapor, and since there is but one component there can be but one degree of freedom.

$$F = C - P + 2 = 1 - 2 + 2 = 1.$$

When there is one degree of freedom, the system is said to be univariant, and it is necessary to specify only one variable — either temperature or pressure, but not both. For example, if it is stated that the system contains both liquid water and water vapor at 25° C., it is not necessary to specify the pressure because it has been found by experiment that water and its vapor can exist together at 25° only under a pressure of 23.7 mm. The pressure at any temperature may be read from the vapor-pressure curve.

The line *CO* is the sublimation curve of ice. Above it lies ice and below it lies vapor. Only along *CO* can ice and vapor exist together in equilibrium. There are two phases here and one component, so there is one degree of freedom.

At the point *O*, the two curves, liquid-vapor and solid-vapor, intersect. There are three phases in equilibrium here, and so it is called a triple point. According to the phase rule there are no degrees of freedom, or in other words the system is invariant:

$$F = C - P + 2 = 1 - 3 + 2 = 0.$$

It is not necessary to specify either temperature or pressure under these conditions, for there is only one possible temperature and one possible pressure which will permit all three phases to exist together in equilibrium. If the temperature is raised, the ice will melt and there will be but two phases; if the temperature is lowered, the liquid water will freeze; if the pressure on the vapor is raised, the vapor will condense; and, finally, if the pressure is lowered, the liquid and ice will evaporate.

The line *OB* shows how the melting-point changes with pressure. At all points on the line the pressure is greater than the vapor pressure, as given by the line *COA*; so it may be concluded that no vapor is present. This line is inclined toward the vertical axis and the melting-point of ice is lowered by increasing the pressure — a fact which can be predicted from the principle of Le Chatelier and from the Clapeyron equation, since the liquid water occupies a smaller volume than the solid ice. Along *OB* there are two phases, ice and liquid water, and therefore one degree of freedom.

Ice and water are in equilibrium with their vapor in air under atmospheric pressure at a temperature of 0° C. The definition of the Centigrade scale depends on this fact. The situation is somewhat complicated because the pressure of water vapor is only 4.57 mm. whereas the total pressure on the ice and water is 1 atmosphere.

If ice and water are allowed to evaporate into a previously evacuated space, the pressure on the ice and water will be 4.57 mm. instead of 1 atmosphere, and the melting-point will be slightly higher. The exact temperature has been found by direct experiment, and also by calculation with the Clapeyron equation, to be 0.0075° C.

The dotted curve *OA'*, which is a continuation of *OA*, represents the vapor pressure of supercooled water. It will be noticed that there is no break in the vapor-pressure curve so long as the solid phase does not separate, and that the vapor pressure of supercooled water, which

is an unstable phase, is greater than that of the stable phase, ice, the same temperature.

The lower limit of the sublimation curve *OC* is theoretically determined by the absolute zero; the vaporization curve *OA* terminates at the critical temperature, 364.3°, corresponding to a pressure of 194.6 atmospheres. Investigations conducted by Tammann* and Bridgman† with a view to determining the upper limit of the fusion curve *OB* have revealed the existence of at least five different crystalline modifications of ice, all of which, with the exception of ordinary ice, are denser than water. The first of these new forms of ice makes its appearance at a pressure of 2115 kilograms per square centimeter, and the last at a pressure of 6380 kilograms.

The System, Sulphur (Rhombic, Monoclinic), Liquid and Vapor. This system is more complicated than the preceding one-component system, since there are two solid phases, in addition to the liquid and vapor phases. At ordinary temperatures, rhombic sulphur is the stable modification. When this is heated rapidly it melts at 115° C., but if it is maintained in the neighborhood of 100° C. it gradually changes into monoclinic sulphur, which melts at 120° C. Monoclinic sulphur can be kept indefinitely at 100° C. without undergoing change into the rhombic modification, or in other words, it is the stable phase at this temperature. It is evident, therefore, that there must be a temperature above which monoclinic sulphur is the stable form, and below which rhombic sulphur is the stable modification. This temperature at which both rhombic and monoclinic modifications are in equilibrium with each other and with their vapor, is termed the *transition-point*. Its value has been determined to be 95.6° C. The change from one form into the other is relatively slow, so that it is possible to measure the vapor pressure of rhombic sulphur up to its melting-point, and that of monoclinic sulphur below its transition-point. The vapor pressure of solid sulphur, although very small, has been measured as low as 50° C.

The complete pressure-temperature diagram for sulphur is shown in Fig. 92. At the point *O*, rhombic and monoclinic sulphur are in equilibrium with sulphur vapor, this being a triple point, analogous to the point *O*, in Fig. 91. The vapor-pressure curves of rhombic and monoclinic sulphur are represented by *OB* and *OA*, respectively. The curve *OA'*, which is a continuation of *OA*, is the vapor-pressure curve of monoclinic sulphur in a metastable region. In like manner, *OB'* represents the vapor-pressure curve of rhombic sulphur in

* Ann. Physik (**4**) **2**, 1424 (1900).

† Proc. Am. Acad., **47**, 411 (1912).

metastable condition, B' being a metastable melting-point. As in the pressure-temperature diagram for water, the metastable phases have the higher vapor pressure. The effect of increasing pressure on the transition-point O is represented by the line OC. This is termed a *transition curve*. Since increase in pressure raises the transition-point, the line OC slopes away from the vertical axis. The effect of increase of pressure on the melting-point of monoclinic sulphur is shown by

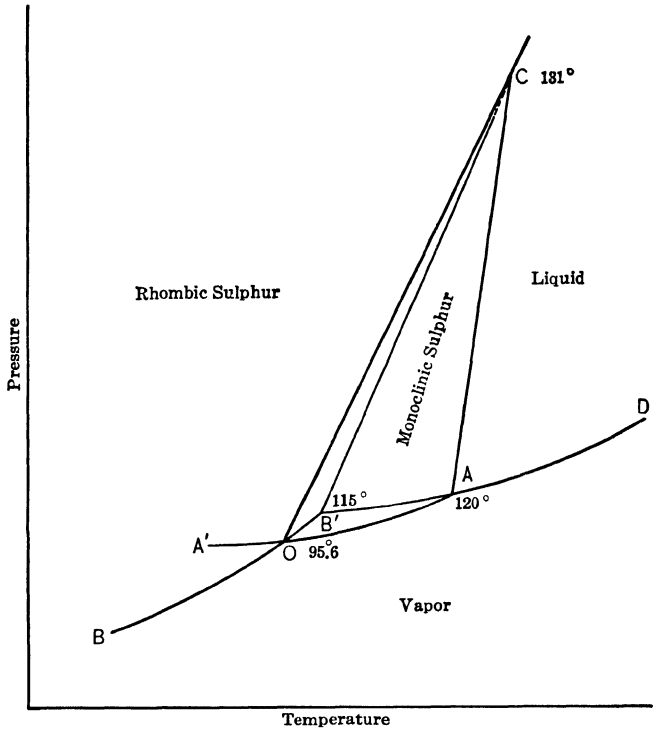


FIG. 92

the curve AC. This also slopes away from the vertical axis, but the change in the melting-point of monoclinic sulphur produced by a given change in pressure being less than the corresponding change in the transition-point, the two curves, OC and AC, intersect at the point C. The point C corresponds to a temperature of 131° C. and a pressure of 400 atmospheres. The vapor-pressure curve of stable liquid sulphur is represented by the curve AD. The vapor-pressure curve of the metastable liquid phase is represented by the curve AB', which is continuous with AD. The diagram is completed by the curve $B'C$, which represents the effect of pressure on the metastable melting-point

of rhombic sulphur. Monoclinic sulphur does not exist above the point C. Hence, when liquid sulphur is allowed to solidify at pressures exceeding 400 atmospheres, the rhombic modification is formed, whereas under ordinary pressures the monoclinic modification appears first.

The phase rule enables us to state the exact conditions required for equilibrium, and to check the results of experiment. Thus, according to the formula, $C - P + 2 = F$, since $C = 1$, the system will be non-variant when $P = 3$. Since there are four phases involved, theoretically any three of these may be co-existent and four triple points are possible. The theoretically possible triple points are as follows:

(1) Rhombic sulphur, monoclinic sulphur, and vapor (O);
(2) Rhombic sulphur, monoclinic sulphur, and liquid (C);
(3) Rhombic sulphur, liquid, and vapor (B');
(4) Monoclinic sulphur, liquid and vapor (A).

In this particular system all four possible triple points can be realized experimentally. That this is the case, is due to the comparative slowness of the change from rhombic to monoclinic sulphur above the transition temperature. If this change were rapid, it is evident that all of the theoretically possible non-variant systems could not be realized experimentally.

As in the case of water, the curves in the diagram represent univariant systems and the areas, bivariant systems. It is a good exercise to tabulate the univariant and bivariant systems represented in the pressure-temperature diagram for sulphur.

Two-Component Systems. When we apply the phase rule to systems of two components, we obtain, $2 - P + 2 = F$, or, in other words, we find that the maximum number of degrees of freedom possible is three. Therefore, in order to represent a two-component system completely, three rectangular coördinate axes, representing temperature, pressure, and concentration, will be required. Such a space model is shown in Fig. 93. In this three-dimensional diagram, any curve, such as AB lying in a P–T plane, represents change of pressure with temperature, the concentration remaining constant; any curve, such as AF lying in the P–C plane, represents change of pressure with concentration, the temperature remaining constant; in like manner, any curve, such as DE lying in a T–C plane, represents change in concentration with temperature, the pressure remaining constant. Any line on any one of the surfaces of the space model represents the simultaneous variation of the three quantities — pressure, temperature, and concentration.

Although three-dimensional models constructed in this manner undoubtedly give the most complete representation of two-component systems, it has been found that the various phase relations can be depicted clearly and satisfactorily by passing planes through such space models, perpendicular to the three coördinate axes. It follows, therefore, that there will be three different sets of such diagrams corresponding to each model; namely, the *P–T* diagrams, the *T–C* diagrams and the *P–C* diagrams. Of these diagrams, the *P–T* and *T–C* diagrams are generally the most important. Among the different types of two-component systems which have been studied may be mentioned systems involving anhydrous salts and water, hydrated salts and water, volatile solutes, two liquid phases, consolute liquids, and solid solutions.

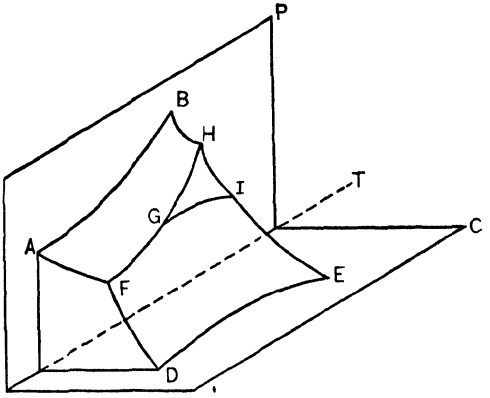


FIG. 93

We shall confine ourselves to the consideration of two-component systems consisting of non-volatile solid solutes and liquid solvents. These systems may be conveniently classified as follows:

Class I. The two components crystallize together as a mixture of the pure components.

Class II. The two components crystallize together forming definite chemical compounds.

Class III. The two components crystallize together forming mixed crystals.

Class I. — KCl + H_2O. Projections of this system onto a *P–T* plane are shown in Fig. 94, together with a diagram for water alone, which is represented by dotted lines. At the triple point, *O*, ice and water have the same vapor pressure. Similarly, a solution at its freezing-point has the same vapor pressure as the ice which separates. The intersection of the vapor-pressure curve of ice, *OB*, and the vapor-pressure curve of the solution of the anhydrous salt, *O''A''*, determines a new triple point *O''*. Since the presence of the dissolved salt tends to diminish the vapor pressure of water, the curve *O''A''* is situated below the curve *OA*, and for the same reason, the triple point *O''* is found to the left of *O*. If an excess of dissolved

substance is present, all the liquid phases which are formed will of necessity be saturated solutions. When these solutions finally freeze, they will furnish, not pure ice, but a mixture of ice and solid salt, known as a *cryohydrate*. By a partial freezing, we can obtain the system: Solid salt, ice, saturated solution and vapor, or in other words, a system of $C + 2$ phases, which can exist only at the freezing temperature of the saturated solution, T', and at the pressure p', corresponding to the

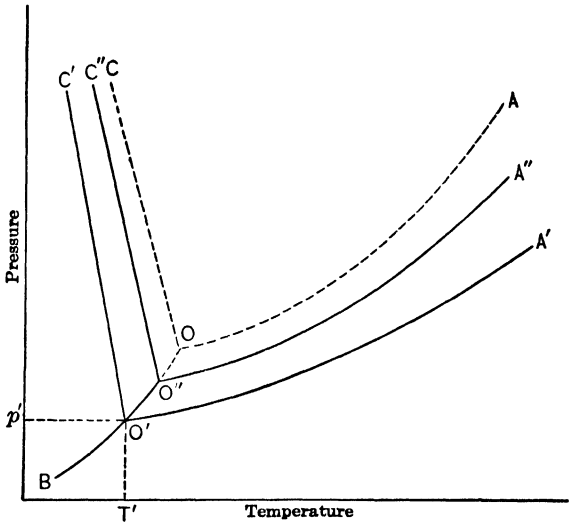


FIG. 94

vapor pressure of ice and that of the saturated solution. These conditions are represented by the quadruple point O'. If we pass from the point O', increasing the temperature and pressure as prescribed by the curve $O'A'$, the ice will disappear, while the salt, the saturated solution, and the vapor will furnish a series of three-phase systems. Again starting from the point O', and lowering the temperature and the pressure, as indicated by the curve $O'B$, the liquid phase will disappear, while the solid salt, ice, and vapor will constitute another series of three-phase systems. This, of course, is on the supposition that the vapor pressure of the solid salt is negligible. Finally, an increase in pressure will cause the disappearance of the vapor phase and a slight lowering of the melting-point of the ice.

All possible non-saturated solutions of the salt will be represented by points within the area, $AOO'A'$. Thus, let $O''A''$ represent the vapor-pressure curve of a dilute aqueous solution of the salt. The freezing-point of this solution is represented by the point O''; $O''C''$

represents the variation of the freezing-point of the solution with pressure. The following table summarizes the possibilities indicated by the phase rule:

(a) Areas. $(C - P + 2 = F)$, $2 - 2 + 2 = 2$, i.e., bivariant systems:

Salt-vapor, below $A'O'B$ and above T-axis,
Solution-vapor, between AO and $A'O'$,
Solution-ice, between CO and $C'O'$,
Ice-salt, between $C'O'B$ and P-axis.

(b) Curves. $(C - P + 2 = F)$, $2 - 3 + 2 = 1$, i.e., univariant systems:

Solution-vapor-salt, $A'O'$,
Solution-ice-salt, $C'O'$,
Ice-salt-vapor, BO',
Solution-ice-vapor, OO'.

(c) Points. $(C - P + 2 = F)$, $2 - 4 + 2 = 0$, i.e., non-variant system, O'.

The P–T projections (Fig. 94) having been discussed, we now turn to the T–C diagram for the same system, Fig. 95. In this diagram, the abscissas represent concentrations, and the ordinates, temperatures. For convenience, corresponding points in Figs. 94 and 95 are designated by the same letters. The equilibrium between ice, water, and water vapor is represented by the point O. As the proportion of salt is increased, the temperature of equilibrium is lowered along the curve OO'. Ultimately, a point will be reached at which the solution becomes saturated, and on further addition of salt it will no longer dissolve but will remain in contact with the ice and saturated solution. This is the cryohydric point, which represents the lowest temperature of freezing obtainable in this particular system. The diagram is completed by the solubility curve of the salt, $O'A'$. Each point on this curve represents the concentration of a saturated solution, down to the cryohydric temperature.

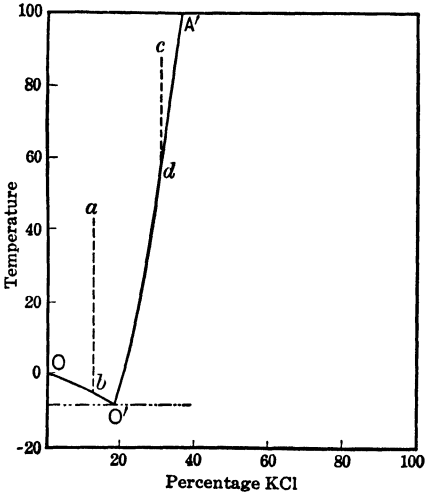


FIG. 95

The meaning of the concentration-temperature diagram may be made clearer by a consideration of the behavior of a solution when gradually cooled. Let *a* represent a dilute solution of the anhydrous salt. On lowering the temperature along *ab*, no change will occur until the curve *OO'* is reached; then, ice will begin to separate, and as the cooling is continued, the composition of the solution will change along *OO'* until it reaches the cryohydric point *O'*. Here, both salt and ice will separate, and the solution will solidify completely at the temperature corresponding to the point *O'*. In like manner, if we start with a concentrated solution, represented by the point *c*, and cool along *cd*, no change will take place until the curve *O'A'* is reached; then solid salt will separate and the composition of the solution will alter along *O'A'*, until the temperature is reduced to that corresponding to the cryohydric point, when the whole solution will solidify as in the previous case.

This phenomenon was first systematically investigated by Guthrie,* who concluded that such mixtures having constant composition and definite melting-point, are chemical compounds. Therefore, he proposed to call them cryohydrates. It has since been shown that cryohydrates are not definite chemical compounds. Among the various reasons which have been advanced to prove the incorrectness of Guthrie's views, the following are the most convincing: — (1) the physical properties of a cryohydrate are the mean of the corresponding properties of the constituents — a fact rarely true of chemical compounds; (2) the lack of homogeneity of a cryohydrate can be detected under the microscope; and (3) the constituents are seldom present in simple molecular proportions.

Class II. — $FeCl_3 + H_2O$. An interesting example of this class of two-component systems is furnished by mixtures of ferric chloride and water. This system has been very carefully investigated by Roozeboom.† The concentration-temperature diagram, plotted from Roozeboom's data, is given in Fig. 96. The freezing-point of pure water is represented by *A*, and the lowering of the feezing-point produced by the addition of ferric chloride is indicated by the curve *AB*. At the cryohydric temperature, $-55°$ C., ice, $Fe_2Cl_6 \cdot 12\ H_2O$, saturated solution, and vapor are in equilibrium, and the system is non-variant. On adding more ferric chloride, the ice phase disappears, and the univariant system, $Fe_2Cl_6 \cdot 12\ H_2O$, saturated solution, and vapor results. The equilibrium is represented by the curve *BC*, which may be regarded as the solubility curve of the dodecahydrate. On continuing the addition

* Phil. Mag., [5] **2**, 211 (1876).

† Z. physik. Chem., **4**, 31 (1889); **10**, 477 (1892).

of ferric chloride, the temperature of equilibrium rises until the point *C* is reached. Here the composition of the solution is identical with that of the dodecahydrate, and, therefore, the temperature corresponding to this point, 37° C., may be looked upon as the melting-point of $Fe_2Cl_6 \cdot 12\,H_2O$. Further addition of ferric chloride will naturally lower the melting-point, and the equilibrium will alter along the curve *CD*. It is thus possible to have two saturated solutions

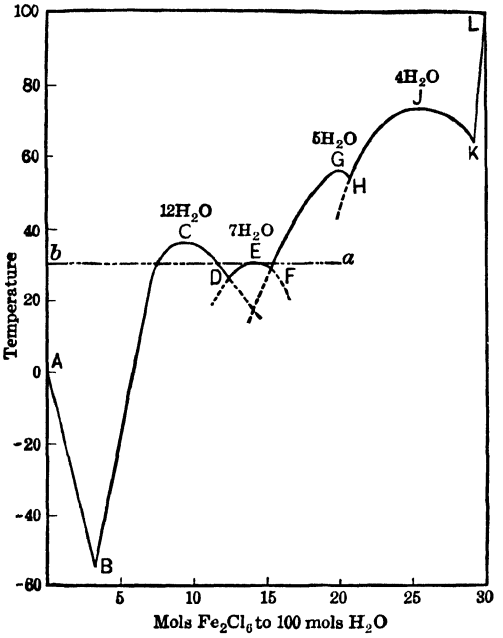


FIG. 96

(at the same temperature) one of which contains more water, and the other less, than the hydrate which is in equilibrium with the solution. At the point *D*, the curve reaches another minimum, which is analogous to the point *B*, except that the heptahydrate, $Fe_2Cl_6 \cdot 7\,H_2O$, takes the place of ice. Here we have equilibrium between the dodecahydrate, the heptahydrate, saturated solution, and vapor, and the system is non-variant. On further addition of ferric chloride, another maximum is reached at *E*, corresponding to the melting-point of the heptahydrate. In a similar manner, two other maxima at greater concentrations of ferric chloride, reveal the existence of the hydrates, $Fe_2Cl_6 \cdot 5\,H_2O$, and $Fe_2Cl_6 \cdot 4\,H_2O$. At the three remaining quadruple points the following phases are in equilibrium: At *F*, $Fe_2Cl_6 \cdot 7\,H_2O$,

$Fe_2Cl_6 \cdot 5\,H_2O$, saturated solution and vapor; at H, $Fe_2Cl_6 \cdot 5\,H_2O$, $Fe_2Cl_6 \cdot 4\,H_2O$, saturated solution and vapor; and at K, $Fe_2Cl_6 \cdot 4\,H_2O$, Fe_2Cl_6, saturated solution and vapor. The solubility of the anhydrous salt is represented by the curve, KL. Metastable solubility and melting-point curves are represented by dotted lines.

It is a good exercise to apply the phase rule to this system. If a fairly dilute solution of ferric chloride is evaporated at 31° C., the water gradually disappears, and a residue of the dodecahydrate remains. This residue then liquefies, and again dries down, the composition of the residue corresponding to the heptahydrate: on further standing, the phenomenon is repeated, the final and permanent residue having a composition corresponding to the pentahydrate. The dotted line, *ab*, shows the isothermal along which the composition varies. It would have been a difficult matter to explain the alternations of moisture and dryness, observed in this experiment, without the concentration-temperature diagram.

Class III. — In all the two-component systems thus far considered, the composition of the solid phase has remained constant, while that of the liquid phase has undergone continuous variation. In the systems belonging to Class III, however, the solid phase which separates from the solution, on cooling, is found to contain both components in continuously varying proportions. It follows, therefore, that two-component systems belonging to this class consist of *two* solutions, one a *liquid solution* and the other a *solid solution*, in equilibrium with each other. Obviously, the complete temperature-concentration diagram must contain two curves, one of which corresponds to the liquid and the other to the solid solution. The upper curve, corresponding to the liquid solution, is called the crystallization-point curve; the lower curve, corresponding to the solid solution, is known as the melting-point curve. The region above the curves represents liquid solutions; the region below the curves represents solid solutions. There are three distinct types of melting-point curves for solid solutions in which the two components are miscible in all proportions: namely,

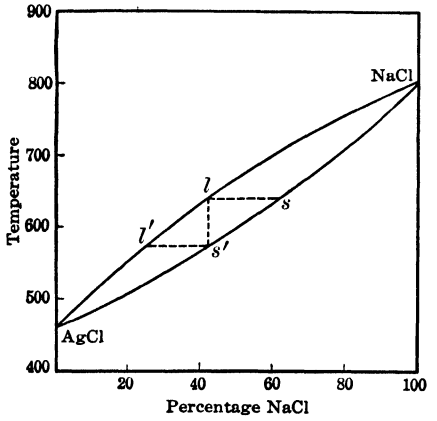


FIG. 97

Type I, in which the freezing-points of all mixtures lie between those of the two components; Type II, in which a certain mixture has a maximum freezing-point; and Type III, in which a particular mixture has a minimum freezing-point.

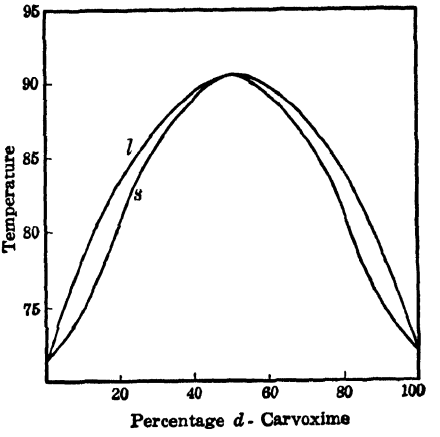


FIG. 98

The general characteristics of a two-component system belonging to Type I may be illustrated by the temperature-concentration diagram of the system AgCl–NaCl, as shown in Fig. 97. If the temperature of a fused mixture of these two salts, having the composition represented by the point l on the crystallization-point curve, is gradually lowered, a solid phase, having the composition represented by s, will separate out. If the temperature is lowered very slowly, so as to insure the homogeneity of the solid phase, the composition of the final portion of the solution to solidify will correspond to that of the point l', and the composition of the solid with which it is in equilibrium will be represented by s'. If care is not taken to cool the solution gradually, the solid phase will not become homogeneous, owing to the slow rate of diffusion of the two components in the mixture, and consequently the final temperature of solidification will be considerably lower than that corresponding to the point s'. This precaution is of great practical importance in connection with the preparation of alloys, where the rate of diffusion of the constituents is necessarily slow.

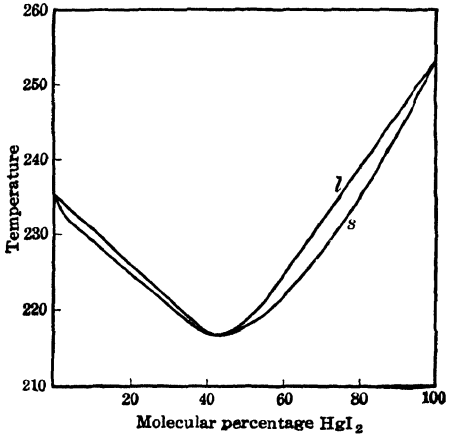


FIG. 99

Illustrations of the two remaining types of binary mixtures which form mixed crystals are shown in the accompanying diagrams. The diagram of the system, *d*- and *l*-carvoxime ($C_{10}H_{14}N.OH$), shown in

Fig. 98,* furnishes an example of Type II; Type III is illustrated by the system $HgBr_2$–HgI_2,† a diagram of which is shown in Fig. 99. It will be seen that the curves shown in Figs. 97, 98 and 99 are exactly analogous to the three types of boiling-point curves of binary mixtures which have been discussed in an earlier chapter (p. 149).

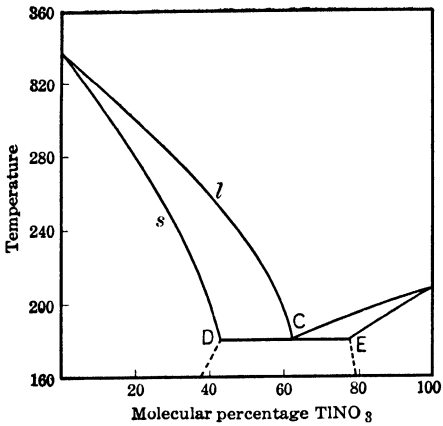


FIG. 100

A large number of binary systems are known in which the two components do not form a continuous series of mixed crystals. This case, which is perfectly analogous to that of the partial miscibility of liquids, may be illustrated by the system, KNO_3–$TlNO_3$, a diagram of which is shown in Fig. 100. At the temperature corresponding to C, two solid solutions having compositions corresponding to D and E separate out, the temperature remaining constant until all the liquid has solidified. On lowering the temperature below C, the two solid solutions, which were in equilibrium at C, undergo a change in composition, as indicated by the dotted lines.

Three-Component Systems. According to the phase rule, the number of degrees of freedom in a three-component system will be given by the expression, $3 - P + 2 = F$. It is evident, therefore, that the system will become invariant when five phases — the maximum number possible in a three-component system — are co-existent. Since at least one phase must be present, the maximum number of degrees of freedom will be four, the variables being temperature, pressure, and the ratios of two of the components to the remaining component in any single phase.

In the graphic representation of three-component systems, use is commonly made of the triangular diagram. This consists of an equilateral triangle, each side of which is divided into one hundred equal parts, corresponding to 100 per cent of each of the three pure components, which are represented by the vertices of the triangle. For example, if it is desired to represent on a triangular diagram, a ternary mixture consisting of x per cent of A, y per cent of B and z per cent of C,

* Adriani, Z. physik. Chem., **33**, 469 (1900).

† Reinders, ibid., **32**, 494 (1900).

we would first measure off on AB, in the triangular diagram shown in Fig. 101, x units from B and y units from A, and then through the points so obtained, draw lines parallel to BC and AC respectively. The point, P, at which these two lines intersect, will represent the ternary mixture having the composition given above. Should it be desired to represent, simultaneously, the variation of the equilibrium with temperature, this can readily be accomplished by plotting the latter on an axis perpendicular to the plane of the triangular diagram.

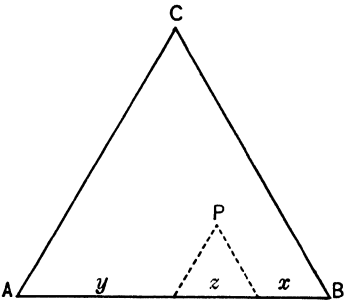


FIG. 101

Owing to the complexity of three-component systems, we shall limit our treatment of these systems to a brief consideration of one or two relatively simple cases in which the conditions are such that only liquid phases are involved.

The system, chloroform-water-acetic acid, which has been thoroughly investigated by Wright,* furnishes an interesting example of a ternary liquid mixture, in which the three components form a single pair of partially miscible liquids. At ordinary temperatures, water and chloroform are only slightly soluble in each other, while each of these liquids is miscible with acetic acid in all proportions. The equilibrium relations in this system, at 18° and under constant pressure, are shown graphically in Fig. 102. Since both temperature and pressure are assumed to be constant, there can be only two degrees of freedom. If we have one homogeneous phase, there will be two degrees of freedom (percentages of two components) represented by any point within the region. If we have two liquid phases there will be one degree of freedom (percentage of one component), represented by some point on the curve aKb. On adding water to chloroform, we obtain a homogene-

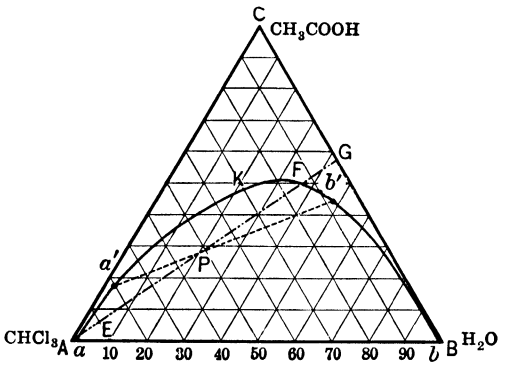


FIG. 102

* Proc. Roy. Soc., **49**, 174 (1891); **50**, 375 (1892).

ous solution, provided the amount of water does not exceed that corresponding to complete saturation, represented by the point a. If further amounts of water are added, the mixture will separate into two layers, one of which consists of a saturated solution of water in chloroform, and the other, a saturated solution of chloroform in water. The composition of these two conjugate solutions is represented by the points a and b. If now, acetic acid is added, it will distribute itself between the two layers, forming two conjugate ternary solutions of chloroform, water and acetic acid which are in equilibrium with each other. These solutions are represented by two points, such as a' and b', within the triangular diagram. The line joining a' and b' is known as a *tie-line*; as is generally the case, this line is not parallel to the base of the triangle ABC. As more and more acid is added, the tie-lines become shorter and shorter, and ultimately, when the compositions of the two conjugate solutions become identical, they shrink to the single point, K. The point K is, therefore, a *critical point*, since further addition of acetic acid will result in the formation of a single homogeneous phase. Any point within the curve represents a ternary mixture which will separate into two conjugate liquid phases, while any point without the curve represents a single homogeneous liquid phase.

A ternary mixture whose composition is represented by the point P, will separate into two conjugate ternary solutions having the compositions, a' and b'. If a line is drawn from A through P, cutting the isotherm aKb in E and F, and the line BC in G, it can be shown, that in all mixtures represented by points on AG, the ratio of the components, B and C, is constant, and equal to GB/GC. If to a mixture of water and acetic acid whose composition is represented by the point G, increasing amounts of chloroform are added, we shall obtain in succession, (1) a series of homogeneous solutions between G and F, (2) a series of heterogeneous mixtures of two conjugate solutions between F and E, and (3) another series of homogeneous solutions between E and A.

Owing to the fact that acetic acid does not distribute itself equally between water and chloroform, the critical point K lies below the highest point of the curve.

We shall now consider, very briefly, two other typical three-component systems, involving two and three pairs of partially miscible liquids, respectively.

The system water-aniline-phenol, which has been investigated by Schreinemakers,* may be taken as an example of a three-component

* Z. physik. Chem., **29**, 577 (1899).

system containing two pairs of partially miscible liquids, namely water and aniline, and water and phenol. This system is represented, diagrammatically, in Fig. 103, three different isothermals being given.

The system, water-ether-succinic nitrile, also investigated by Schreinemakers,* furnishes an example of a three-component system containing three pairs of partially miscible liquids. This system is represented in the diagram shown in Fig. 104. The compositions of all mixtures forming single homogeneous solutions are represented by points in the unshaded areas of the triangular diagram. All points lying within the shaded quadrilateral areas represent mixtures which

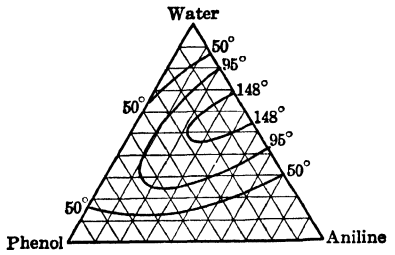


FIG. 103

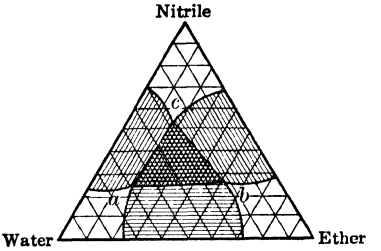


FIG. 104

form two liquid layers; all points included within the shaded triangular area represent mixtures which break up into three liquid layers of the composition *a*, *b* and *c*.

Alloys. The phase rule has proven to be of inestimable value in the investigation of intermetallic mixtures, commonly known as *alloys*. In the study of these substances, the determination of the freezing-point curve is of fundamental importance, since, from its characteristics, an insight into the nature of the solid and liquid phases involved can generally be obtained. It has already been pointed out, that the freezing-point curves of two-component systems may conveniently be divided into the three following types: — Type I, in which the pure components separate out from the mixture; Type II, in which the components form one or more compounds with each other; and Type III, in which the components form mixed crystals. Representatives of each of these types are found among the alloys.

Owing to the fact that the temperatures at which most alloys melt are relatively high, and also because of the difficulty of bringing about the separation of the different solid phases free from contamination with the other phases, it is customary to employ the method of *thermal analysis* in the investigation of the freezing-points of alloys. This

* Z. physik. Chem., **25**, 543 (1898).

method is based upon the experimental determination of the cooling curves of molten mixtures of the given metals in varying proportions. The curve obtained by plotting temperature against time, when a two-component liquid system is allowed to cool slowly by radiation, is called the *cooling curve.* This curve is logarithmic when the temperature of the environment is constant, but becomes rectilinear if the surrounding temperature is regularly and progressively lowered. So long as the system consists of a single liquid phase, the cooling curve will remain smooth and continuous, as shown by AB in Fig. 105*a*, but should a second phase appear, a sudden discontinuity in the curve will occur simultaneously, as shown by BC in the diagram. If the new phase has the same composition as the liquid phase, the temperature will remain constant, as in the diagram, until all of the liquid phase has disappeared. On the other hand, if the new phase differs in composition from that of the liquid phase, the cooling curve will undergo a somewhat abrupt change in direction, due to the fact that the composition of the liquid phase alters continuously as the temperature falls. If a third phase is formed, the temperature of the system will remain constant until one of the phases has completely disappeared. The cooling curve of a two-component liquid system, in which the first phase to separate has a different composition from that of the liquid phase, is shown in Fig. 105*b*. Here EF represents the cooling curve of the liquid; F, the appearance of the second phase differing in composition from that of the liquid phase; and H represents the appearance of a third phase. During the separation of the latter, the temperature of the system remains constant, after which it cools uniformly along IK.

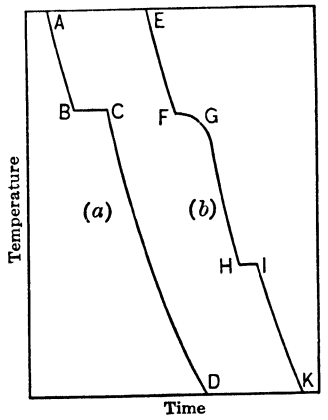


FIG. 105

The System, Zinc-Cadmium. A brief consideration of the two-component system, zinc-cadmium, will serve to illustrate the application of the method of thermal analysis to the study of alloys. In this system, the two components are not miscible in the solid state and do not form intermetallic compounds. In order to determine the curves of equilibrium, mixtures of the two metals, in varying proportions, are fused, and then allowed to cool slowly, the rate of cooling being measured by means of a thermocouple, one junction of which is maintained

at constant temperature, while the other junction is placed in the mixture. The terminals of the thermocouple are connected to a sensitive galvanometer, graduated to read directly in degrees, and the rate of cooling is followed by the movement of the needle of the galvanometer. The cooling curves, thus obtained, for each of the two components, and for nine mixtures containing increasing amounts of cadmium, are plotted in the diagram, shown in Fig. 106. Let us take, for example, cooling curve No. 2, corresponding to a liquid mixture

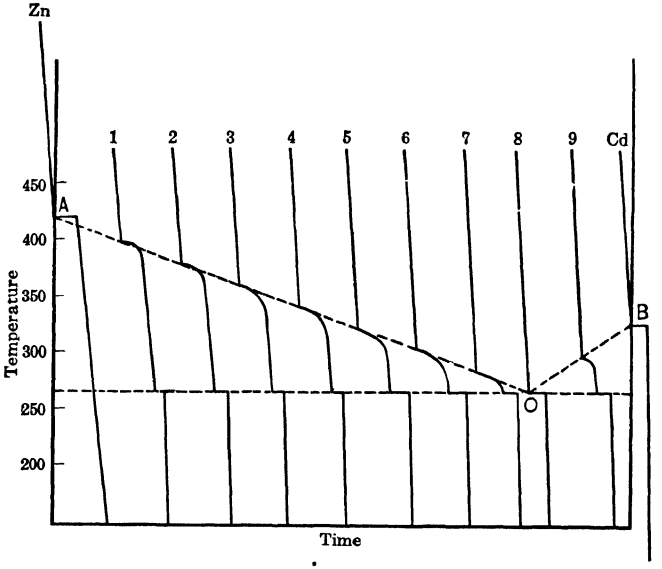


FIG. 106

which is relatively rich in zinc. As the temperature falls, a point will ultimately be reached at which pure zinc begins to crystallize, and since the temperature remains constant during the crystallization, a break occurs in the cooling curve. This first break is the freezing-point of the mixture, and determines a point on the curve *AO*. As zinc continues to separate, the composition of the mixture changes until a second break appears: here the mixture is saturated with respect to cadmium, and both metals separate as a conglomerate, having the same composition as the fused mixture. The separation of the latter phase causes the second break in the cooling curve, the temperature remaining constant until the entire mass has solidified. It will be noticed that this system is the exact analogue of the system — anhydrous salt and water. The point *O*, which corresponds to the cryohydric point, is called the *eutectic point*, and the composition of the

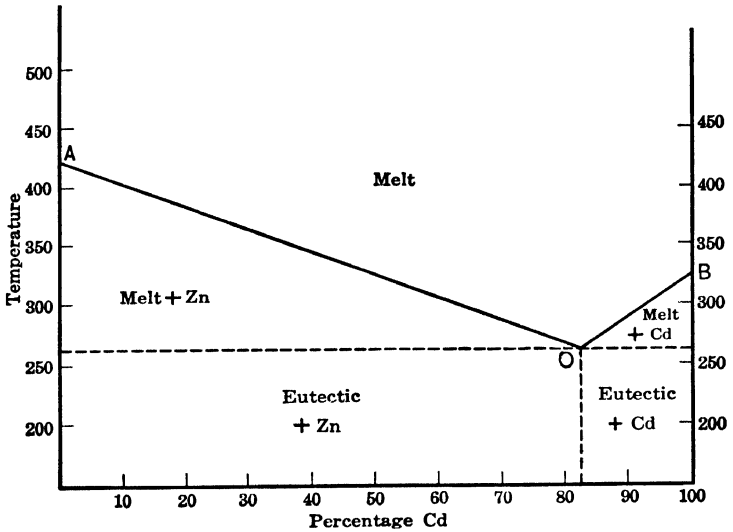


FIG. 107

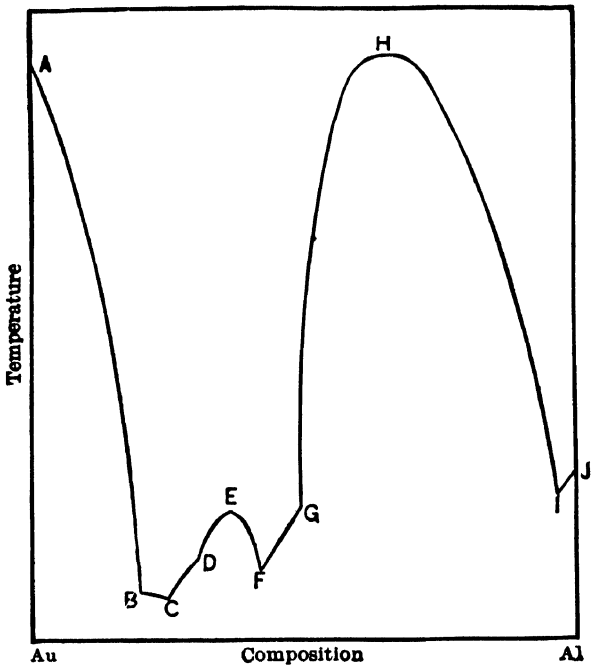


FIG. 108

mixture having this minimum melting-point, is known as the *eutectic mixture.* From the cooling curve diagram we can construct the equilibrium diagram, shown in Fig. 107.

The System, Gold-Aluminum. A binary system belonging to Type II, in which the components form several compounds with each other, is the system, gold-aluminum, which has been studied by Heycock and Neville.* The concentration-temperature diagram of this system, which is shown in Fig. 108, reveals the existence of definite compounds, Au_2Al, and $AuAl_2$, corresponding to the points E and H, respectively. The discontinuities at B, D and G suggest the possibility of other compounds, viz., Au_5Al_2, Au_4Al and AuAl. The diagram shows that the following substances will crystallize in succession from the molten alloy, these being the different solids with which the liquid mixture is saturated in its successive stages of equilibrium:

Curve AB, pure gold at A;
Curve BC, Au_4Al, nearly pure at B;
Curve CD, Au_5Al_2 or Au_8Al_3, nearly pure at D;
Curve DEF, Au_2Al, pure at E;
Curve FG, AuAl, maximum undetermined;
Curve GHI, $AuAl_2$, pure at H;
Curve IJ, Al, pure at J.

The points C, F, and I represent non-variant systems, the melting-points of the respective eutectic alloys being 527°, 569°, and 647°. This system in many respects resembles the system — ferric chloride and water.

For a further discussion of the phase rule and its applications, the student must consult the references listed below.

REFERENCES

The Phase Rule and its Applications. Findlay.
The Phase Rule. Bancroft.
Physical Chemistry of the Metals. Schenck. Translated by Dean. Chapters II and III.
Metallic Alloys. Gulliver.
Metallography. Desch. Chapters II to V inclusive.
The Crystallization of Iron and Steel. Mellor.
Treatise on Physical Chemistry. Taylor. Chapter IX.
Equilibria in Saturated Salt Solutions. Blasdale.

* Trans. Roy. Soc., **A 194**, 291 (1900).

PROBLEMS

1. The vapor pressure of solid NH_4HS at 25.1° is 50.1 cm. Assuming that the vapor is practically completely dissociated into NH_3 and H_2S, calculate the total pressure at equilibrium when solid NH_4HS is allowed to dissociate at 25.1° in a vessel originally containing ammonia at a pressure of 32 cm. *Ans.* 59.44 cm.

2. At 24.91° the dissociation pressure of ammonium carbamate is 88.3 mm. Calculate the partial pressure of carbon dioxide in a vessel to which an excess of solid ammonium carbamate was added, provided that the vessel originally contained ammonia at a partial pressure of 138.7 mm.

3. In the partition of acetic acid between CCl_4 and water, the concentration of the acetic acid in the CCl_4 layer was c gram-molecules per liter and in the corresponding water layer w gram-molecules per liter.

c	0.292	0.363	0.725	1.07	1.41
w	4.87	5.42	7.98	9.69	10.7

Acetic acid has its normal molecular weight in aqueous solutions. From these figures show that, at these concentrations, the acetic acid in the carbon tetrachloride solution exists as double molecules.

4. Jakowkin determined, analytically, the total chlorine in each layer of a mixture of water and carbon tetrachloride. At 0° he obtained the following results in which concentrations are given in millimols per liter.

Conc. in H_2O layer	58.21	23.08	10.10
Conc. in CCl_4 layer	803.3	222.5	52.93
x	0.3185	0.5180	0.7320

The values of x represent the fraction of chlorine in the water layer which has reacted according to the reaction $Cl_2 + H_2O \leftrightarrows HCl + HClO$.

(*a*) Calculate the distribution ratios from the data of the first two rows.

(*b*) Calculate the distribution ratios, after making a correction for the chlorine that has disappeared through chemical reaction with the water.

5. The distribution coefficient at 25° of lactic acid between water and chloroform (C_{CHCl_3}/C_{H_2O}) expressed in mols per liter is 0.0203.

(*a*) How much lactic acid will be extracted from 100 cc. of a 0.5 molar solution of lactic acid in chloroform by shaking with 200 cc. of water?

(*b*) How much will be extracted if the 200 cc. of water is used to make two extractions, 100 cc. at a time?

6. (*a*) From two of the values given for the dissociation pressures of calcium carbonate calculate the heat of dissociation.

(*b*) What is the partial pressure of carbon dioxide which is in equilibrium with calcium carbonate at 100° C.?

7. The salt $Na_2HPO_4 \cdot 12\ H_2O$ has a vapor pressure at 15° of 8.84 mm., and at 17.3° of 10.53 mm. Calculate the heat of vaporization, i.e., the thermal change during the loss of 1 mol of water of crystallization by evaporation. *Ans.* 12,650 cal.

8. At 49.5° the solubility of *o*-nitrobenzoic acid is 1.88 g. per 100 g. of water; at 75.3° it is 10.48 g. per 100 g. water. (*a*) What is the solubility at 25°?

9. The dissociation pressures of $ZnCl_2 \cdot 2\ NH_3$ are as follows:

T	400.6°	429.1°	457.6°	483.9°
p	0.000061	0.000725	0.00667	0.039 atmos.

Plot log p against $1/T$ and determine the heat of dissociation.

10. Mercuric oxide dissociates according to the reaction, $2\ HgO = 2\ Hg + O_2$.

At 420° C. the dissociation pressure is 387 mm. and at 450° it is 810 mm. Calculate (*a*) the dissociation constants, and (*b*) the heat of dissociation.

Ans. (*b*) 36,770 calories per mol.

11. The following dissociation pressures of mercuric oxide are given by Taylor and Hulett:

360°	390°	420°	450°	480° C.
90	180	387	810	1581 mm.

(*a*) Construct a phase rule diagram which gives the regions in which mercuric oxide decomposes and the regions where it is stable.

(*b*) At what temperature does mercuric oxide begin to decompose in air at 1 atmosphere pressure? *Ans.* (*b*) 426° C.

12. Which has the greater density, (*a*) monoclinic sulphur or rhombic sulphur; (*b*) rhombic sulphur or liquid sulphur; (*c*) monoclinic sulphur or liquid sulphur?

13. The vapor pressure of solid iodine at 50° is 2.16 mm.; at 114.15°, the triple point, it is 90.1 mm. The vapor pressure of liquid iodine at 150° is 294 mm. Above the triple point the melting-point of solid iodine changes only slightly with increase in pressure. Construct a rough phase-rule diagram for iodine, discuss the sublimation of iodine, and state under what conditions liquid iodine may be obtained.

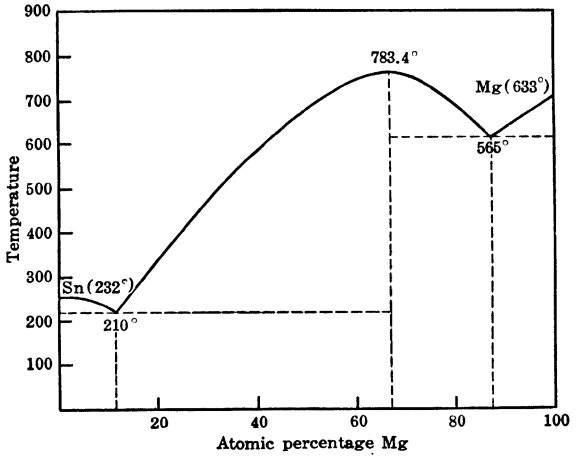


FIG. 109

14. Interpret the temperature-composition diagram for the system, tin-magnesium, shown in Fig. 109.

15. Sketch a phase-rule diagram for thallium and mercury based on the following facts: Mercury melts at −40.0° C.; the compound Tl_2Hg_5 melts at 15° C.; thallium melts at 310° C.; thallium lowers the freezing-point of mercury down to a minimum of −60° at a composition of 8 per cent thallium; the eutectic point for Tl and Tl_2Hg_5 is 0.4° C. at a composition corresponding to 41 per cent thallium.

16. Interpret the temperature-composition diagram for the system, copper-manganese, shown in Fig. 110.

17. Interpret the aniline-water-phenol diagram shown in Fig. 103.

18. Interpret the three-dimensional model representing the system aniline-sulphur dioxide, as worked out by Hill and shown in Fig. 111. (J. Am. Chem. Soc., **53**, 2598 (1931).)

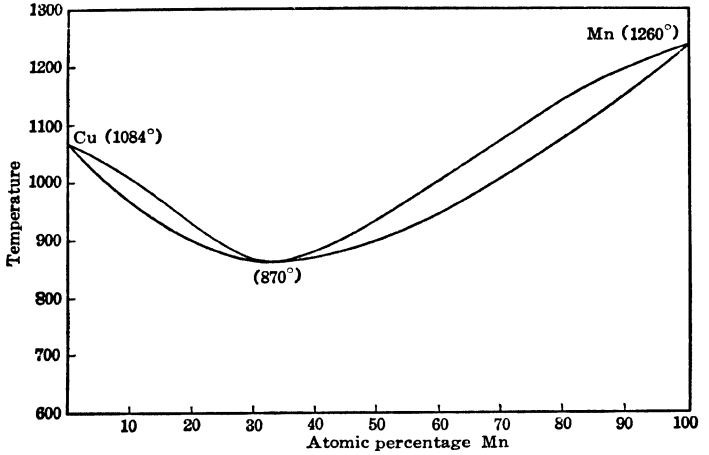


FIG. 110

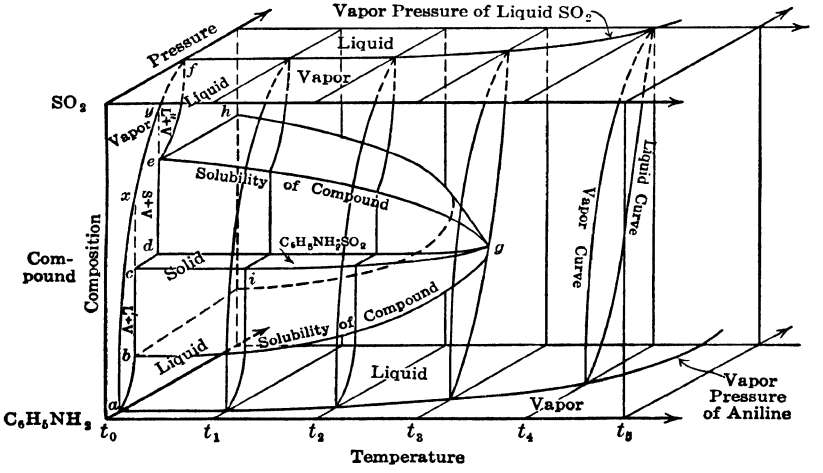


FIG. 111

CHAPTER XIV

CHEMICAL KINETICS

Importance. In the chapters which have gone before we have studied the question of how far a chemical reaction will go, but nothing has been said as to how fast it will go. It has been shown that the equilibrium constant can be calculated very simply from a knowledge of the free energy change involved in the reaction. In a later chapter methods will be given for determining these free energy changes; but none of these thermodynamical considerations has anything to do with time, nor with the mechanism by which the reaction proceeds. They are concerned only with the initial and final states.

Chemical kinetics is concerned with the velocity of reactions and with the intermediate steps by which the final result is obtained. On account of the increase in the number of variable factors, the problems of kinetics are much more difficult and our knowledge of the field is more limited than in thermodynamics. However, the mere fact that the study of kinetics is a pioneer field adds interest to the subject.

We are able to describe mathematically the behavior of a few simple reactions but we have very few generalizations, aside from the mass law, which are useful in predicting in advance the velocity of a given reaction. Moreover, many processes involve two or more reactions which are going on simultaneously in a very complicated manner. Impurities and traces of catalysts are apt to change the velocities so that it is often difficult to obtain reproducible results. In fact it must be admitted that, in governing the velocity of reactions for practical purposes, the art is far ahead of the science.

Inorganic chemistry, in general, is not much concerned with kinetics because most of the reactions are ionic reactions which take place almost instantly. A few inorganic reactions, such as oxidations with oxygen and thermal decompositions, occur with measurably slow velocities. Organic chemistry, on the other hand, is greatly concerned with kinetics. If two or three organic substances are mixed together, there may be dozens of different products which are possible according to thermodynamics. *The product which will predominate is the one which is produced by the fastest reaction.* By altering the concentrations and the temperature and by using specific catalysts, it is possible to bring about a desired reaction. If the desired reaction cannot be

made much faster than all the other possible reactions, the yield is low.

It may be stated at the start that there is no apparent relation between reaction rate and chemical affinity. For example, the polymerization of nitrogen dioxide to nitrogen tetroxide is a mild reaction involving only 14,600 calories per mol, and yet it takes place so rapidly that its rate has not yet been measured. On the other hand a violent reaction like the union of hydrogen and oxygen to give a mol of water, involving a free energy decrease of 56,560 calories, proceeds with immeasurably slow velocity at room temperature in the absence of a catalyst. The ratio of the velocity constants of the forward and the reverse reactions determines the equilibrium constant, but the equilibrium constant tells nothing of the absolute velocities.

Unimolecular Reactions. Mathematical Treatment. Unimolecular reactions are the simplest to describe in mathematical terms, but they are more difficult to explain chemically. In a unimolecular reaction only one substance reacts and its rate of decomposition is directly proportional to its concentration. Mathematically expressed

$$-\frac{dc}{dt} = kc \tag{1}$$

where c is the concentration of material, k is a proportionality factor, and $-dc/dt$ is the rate at which the concentration decreases. This is one expression of the compound-interest law or the law of exponential growth. This law is met with frequently in physical and chemical phenomena, as for example in the absorption of light (p. 102).

Integrating this simple differential equation,

$$-\ln c = kt + \text{constant} \tag{2}$$

$$\log c = -\left(\frac{k}{2.303}\right)t - \text{constant}. \tag{3}$$

It is evident from this equation that in a unimolecular reaction a straight line is produced when the logarithm of the concentration is plotted against time. The velocity constant k can be evaluated by multiplying the negative of the slope of the line by 2.303.

Integrating equation (1) between the limits, concentration c_1 at time t_1, and c_2 at a later time t_2, we have

$$-\int_{c_1}^{c_2}\frac{dc}{c} = k\int_{t_1}^{t_2} dt \tag{4}$$

$$-\ln c_2 - (-\ln c_1) = k(t_2 - t_1)$$

$$k = \frac{2.303}{t_2 - t_1}\log\frac{c_1}{c_2}. \tag{5}$$

This equation may be modified to give the following equation:

$$k = \frac{2.303}{t} \log \frac{c_0}{c} \tag{6}$$

where c_0 is the concentration at the beginning of the reaction when the time is zero and c is the concentration after time t has elapsed.

Still another modification is often used, as shown in equation (7), where a is the initial concentration, x is the amount reacting in time t, and $a - x$ is the concentration remaining after time t.

$$k = \frac{2.303}{t} \log \frac{a}{a - x}. \tag{7}$$

Here k is called the velocity constant, or better, the *specific reaction rate.* It has the dimensions of a number per unit of time and may be expressed in reciprocal seconds, or in other units of time. When, for example, k has a value of 0.001, the material is decomposing at a rate of $\frac{1}{10}$ of 1 per cent per second.

Reaction rates may be described by giving the numerical value of k, or sometimes by giving the period of half-life — i.e., the time necessary for half of a given quantity of material to decompose. It is meaningless to speak of the time necessary for all of the material to decompose, because, theoretically, an infinite time is required. The period of half-life, $t_{\frac{1}{2}}$, is given by equation (8).

$$k = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{1}{\frac{1}{2}} = \frac{2.303}{t_{\frac{1}{2}}} \times \log 2$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}. \tag{8}$$

Unimolecular Reactions. Experimental Data. The calculation of unimolecular reaction rates may be illustrated with the decomposition of nitrogen pentoxide.* Nitrogen pentoxide is a crystalline solid with a high sublimation pressure. It decomposes completely in the gas phase or when dissolved in inert solvents, at a rate which is conveniently measured at room temperature. It is strictly unimolecular and its rate of decomposition has been checked in many different laboratories. The end products are oxygen and a mixture of N_2O_4 and NO_2. The following equation represents the total reaction (but not the intermediate steps):

$$N_2O_5 \rightarrow 2\ NO_2 + \tfrac{1}{2}\ O_2$$
$$\downarrow\uparrow$$
$$N_2O_4$$

* Daniels and Johnston, J. Am. Chem. Soc., **43**, 53 (1921); Eyring and Daniels, J. Am. Chem. Soc., **52**, 1472 (1930).

For every molecule of oxygen produced, two molecules of nitrogen pentoxide have decomposed. The final volume of oxygen, v_∞, when the reaction is completed, is a measure of the original concentration.

When a solution of nitrogen pentoxide in carbon tetrachloride decomposes, the N_2O_4 and NO_2 remain in solution while the oxygen escapes and is measured in a gas burette. The reaction vessel is carefully thermostated and it is agitated to prevent supersaturation. Experimental data at 30° are given in the following table. The final volume of oxygen, v_∞, when the reaction is completed, is a measure of the total amount of nitrogen pentoxide, and the difference between this final volume and the volume v evolved at time t is a measure of the undecomposed nitrogen pentoxide still remaining. It would be possible to convert these volume differences into mols of N_2O_5 by dividing by the factor $(22{,}400 \times 303/273 \times \frac{1}{2})$, but such a conversion is unnecessary in calculating k because the conversion factor cancels out in the unimolecular formulas.

THE DECOMPOSITION OF NITROGEN PENTOXIDE IN CARBON TETRACHLORIDE AT 30° C.

Time (seconds)	$c_{N_2O_5}$ $(v_\infty - v)_{cc}$	log $c_{N_2O_5}$	$k \times 10^5$
0	84.85	1.9287	....
2,400	69.20	1.8401	8.50
4,800	57.20	1.7574	7.93
7,200	47.15	1.6735	8.05
9,600	39.00	.....	x
12,000	32.18	1.5076	8.02
14,400	26.55	1.4240	8.02
16,800	21.85	1.3395	8.11
19,200	18.00	1.2553	8.08
∞	0.00		

In this table the specific reaction rate is calculated by formula (5). The data at 30° are graphed in Figs. 112 and 113. It is evident in Fig. 112 that the concentration, as represented by $v_\infty - v$, is decreasing exponentially with time, and it is apparent from Fig. 113 that a straight line is produced in accordance with equation (3). The constancy of k shown in the table, and the straightness of the line in Fig. 113 are adequate proofs that the reaction is unimolecular.

Many reactions do not give satisfactory constants but these calculations or graphs are useful in determining the order of the reaction. Sometimes it is inconvenient and unnecessary to determine so many

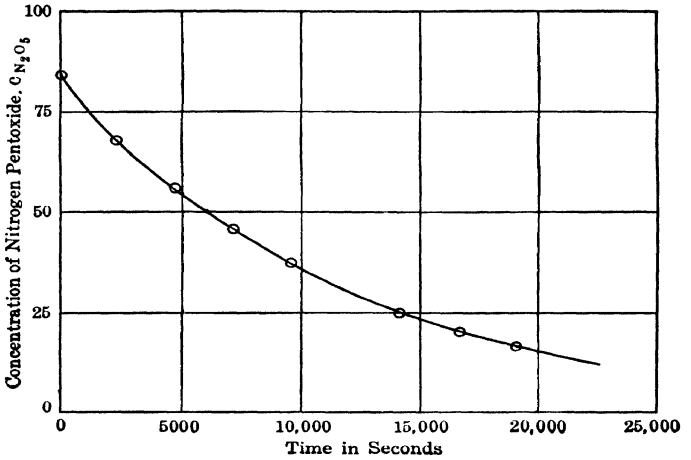


FIG. 112

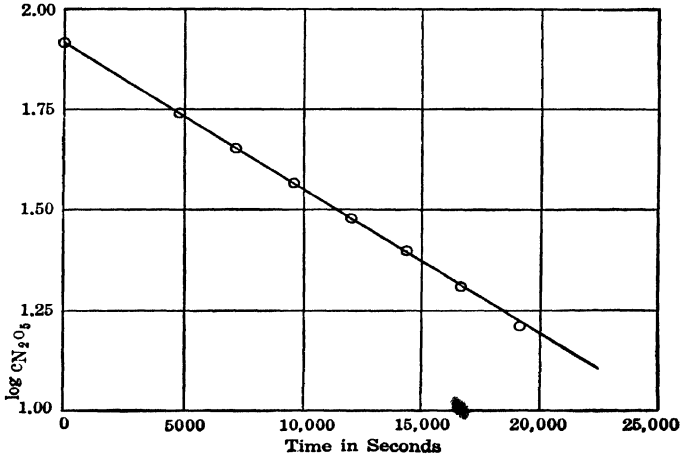


FIG. 113

points on the curve. If the reaction is unimolecular it will take twice as long for three-fourths of the material to decompose as it takes for half of it to decompose. This single criterion is sometimes useful.

After proving that the reaction is strictly unimolecular, the best value of the constant k can be determined from the slope of the straight line, or by substituting two widely separated readings into formula (5). The best results are obtained when the first reading is chosen near the beginning of the experiment, as soon as the reaction vessel has reached the temperature of the thermostat, and the second one when the reaction is about two-thirds completed. In this way the errors of experimental measurement are reduced to a minimum. Two other independent readings over about the same range may be used as a check. It is not satisfactory to average all the constants obtained in successive time intervals with formula (5). Although this procedure has often been followed, it can be shown that it merely cancels out all the intermediate readings and bases the constant only on the first and last readings, which are often the least accurate.*

Bimolecular Reactions. When a reaction depends on the collision between two molecules (of either the same or different species) the reaction is *bimolecular*, or a *reaction of the second order*. Let a and b represent the initial molar concentrations of the two reacting substances, and let x denote the amount transformed in the interval of time t; then the velocity of the reaction will be expressed by the equation,

$$\frac{dx}{dt} = k(a - x)\,(b - x). \tag{9}$$

The simplest case is that in which the two substances are present in equivalent amounts. Under these conditions, the velocity equation becomes,

$$\frac{dx}{dt} = k(a - x)^2. \tag{10}$$

Integrating equation (10), we have:

$$\frac{1}{a - x} = kt + C.$$

Evaluating the integration constant C by setting $x = 0$ when $t = 0$ we have

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}. \tag{11}$$

* Mathematical calculations of reaction rate constants are discussed critically by Roseveare, J. Am. Chem. Soc., **53**, 1651 (1931), and by Reed and Theriault, J. Phys. Chem., **35**, 673 (1931).

If the reacting substances are not present in equivalent amounts, then we must employ the equation

$$\frac{dx}{dt} = k(a - x)\,(b - x). \tag{12}$$

On integrating and evaluating the integration constant by setting $x = 0$ when $t = 0$, this becomes

$$kt = \frac{1}{a - b} \ln \frac{b(a - x)}{a(b - x)}. \tag{13}$$

Or, passing to Briggsian logarithms,

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}. \tag{14}$$

As in the case of a unimolecular reaction the graphical method for obtaining the best value of k is convenient and satisfactory, except in the few cases where the errors of graphing are greater than the experimental error. When $\log \frac{a - x}{b - x}$ is plotted against t, a straight line is obtained if the reaction is bimolecular and k is then obtained by multiplying the slope of the line by $\frac{2.303}{a - b}$.

The value of k, in a bimolecular reaction, is not independent of the units in which the concentration is expressed, as is the case with a unimolecular reaction. Suppose that a unit $1/n$th of that originally selected is used to express concentration, then the value of k in the equation,

$$k = \frac{1}{t} \frac{x}{a(a - x)}$$

becomes

$$k' = \frac{1}{t} \cdot \frac{nx}{na \cdot n(a - x)} = \frac{1}{t} \cdot \frac{x}{na(a - x)}.$$

Thus, the value of k varies inversely as the numbers expressing the concentration. For the sake of uniformity therefore, the value of k should always be calculated using mols per liter as the units of concentration.

As an illustration of a bimolecular reaction, we may take the saponification of an ester by an alkali. The reaction,

$$CH_3COOC_2H_5 + NaOH \rightleftarrows CH_3COONa + C_2H_5OH$$

has been studied by several investigators. Reactions of this type may be followed in a number of different ways. Solutions of ester and

alkali, placed in separate flasks, are warmed to 25° C. in a thermostat maintained at that temperature; equal volumes are then mixed and, at frequent intervals, a portion of the reaction mixture is removed, discharged into standard acid and back-titrated with standard alkali. A final titration after the reaction is completed is necessary to determine the initial concentrations. The most accurate method of following the reaction is by measuring the change in the electrical conductance of the system starting with equal concentrations of alkali and ester. The accompanying tables contain some of the results obtained by Walker* using this method. The temperature of the thermostat was 25° C. and the solutions were $M/100$ with respect to both NaOH and ester.

SAPONIFICATION OF ETHYL ACETATE AT 25° C.

t (min.)	x (mols)	k
0	0.00000	. ....
5	0.00245	6.49
7	0.00313	6.51
9	0.00367	6.45
11	0.00414	6 42
13	0.00459	6.52
15	0.00496	6.50
18	0.00540	y
20	0.00566	6.52
25	0.00615	6.42
27	0.00637	6.50
33	0.00680	6.44
37	0.00704	6.44
∞	0.01000	.....
	Ave.	6.47

SAPONIFICATION OF METHYL ACETATE AT 25° C.

t (min.)	x (mols)	k
0	0.00000	.....
3	0.00260	11.71
4	0 00317	11.60
5	0.00366	11.55
6	0.00411	11.63
7	0.00450	11.69
8	0.00481	11.59
10	0.00536	11.55
12	0.00584	z
15	0.00637	11.70
18	0.00681	11.86
21	0.00712	11.77
25	0.00746	11.75
∞	0.01000	.....
	Ave.	11.64

The number of mols of sodium hydroxide or ester, which has reacted in time t, is represented by x in the second column.

Reicher† investigated the same reaction, when the reacting substances were not present in equivalent proportions. In this work he showed experimentally that the same value of the constant k is obtained, whether excess of NaOH, or of ester, is employed. In this case, the progress of the reaction was followed by the titration method previously mentioned.

* Proc. Roy. Soc. **A 78**, 157 (1906).

† Lieb. Ann., **228**, 257 (1888).

It is now well established that the reaction involves the *hydroxyl ions* rather than the sodium hydroxide molecules, and the reaction may be written

$$CH_3COOC_2H_5 + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + C_2H_5OH.$$

In dilute solutions of barium hydroxide the rate of saponification follows the bimolecular equation, whereas a termolecular reaction might be expected if the reaction involved a combination of a barium hydroxide molecule with two molecules of ethyl acetate.

Termolecular Reactions. Only a few termolecular reactions are known, because they involve a simultaneous collision of three molecules and triple collisions are very rare.

If the initial concentrations of the reacting substances are denoted by a, b and c, and if x denotes the concentration of each which is transformed in the interval of time t, the velocity of the reaction will be represented by the differential equation

$$\frac{dx}{dt} = k(a - x)\,(b - x)\,(c - x). \tag{15}$$

If the substances are present in equivalent amounts, the equation becomes

$$\frac{dx}{dt} = k(a - x)^3, \tag{16}$$

which on integrating and eliminating the integration constant becomes

$$k = \frac{1}{t}\,\frac{x\,(2\,a - x)}{2\,a^2(a - x)^2}. \tag{17}$$

If two molecules of one substance react with one molecule of another in a termolecular reaction, equation (15) becomes

$$\frac{dx}{dt} = k(a - 2\,x)^2\,(b - x), \tag{18}$$

where x denotes the amount of b which is transformed in time t.

The oxidation of nitric oxide

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

is a good example of a termolecular reaction, which has been studied exhaustively by Bodenstein* and by Hasche and Patrick.†

* Z. physik. Chem., **100**, 68 (1922).

† J. Am. Chem. Soc., **47**, 1207 (1925).

First Order Reactions. Many reactions appear to follow the unimolecular equation when in reality the reaction is not unimolecular. They are called *first order reactions*. A case in point is the inversion of cane sugar, which proceeds according to the following equation when free acid is present:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{glucose}}{C_6H_{12}O_6}$$

Although water takes an active part in this reaction, its concentration does not appear to change, because the water is present in large excess. For example, in an 0.5 molal solution there are 111 molecules of water to every molecule of sugar, and when the sugar has completely reacted, the water will have been reduced by less than 1 per cent. The bimolecular equation (9) reduces to the unimolecular equation (1) if $(b - x)$ is constant.

The progress of this reaction may be followed very easily with a polarimeter. Sucrose is dextro-rotatory, but fructose rotates the plane of polarized light more strongly to the left than glucose rotates it to the right. Therefore, as the hydrolysis proceeds, the angle of rotation to the right steadily diminishes and at the end of the reaction the plane of polarization is rotated slightly to the left. For this reason the hydrolysis of cane sugar is commonly termed *inversion*.

If α_0 denotes the initial angle of rotation and α_∞ the angle of rotation when inversion is complete, $\alpha_0 - \alpha_\infty$ as read on the polarimeter is a measure of the total amount of sugar. If α is the angle at time t, the sucrose remaining unhydrolyzed is proportional to $\alpha - \alpha_\infty$. Substituting in equation (6)

$$k = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}. \qquad (19)$$

In applying this formula, the final angle α_∞ must be given its negative sign, i.e. $[\alpha_0 - (-\alpha_\infty)]$.

The following table* gives the results obtained with a 20 per cent solution of cane sugar in an 0.5 molar solution of hydrochloric acid at 25° C.

The decomposition of hydrogen peroxide represents another type of pseudo-unimolecular reaction. Hydrogen peroxide is fairly stable in the absence of catalysts but when it combines with a substance such as ferric chloride, probably to give ferric acid, the decomposition is rapid. Although the reaction involves two reacting substances, one of them (the ferric chloride) is released unchanged after the reaction. The concentration of the ferric chloride remains constant and again equa-

* Experimental results of W. L. Roberts, University of Wisconsin.

HYDROLYSIS OF CANE SUGAR

Time (min.)	a_t	k	Time (min.)	a_t	k
0	6.60	....	95	3.27	0.00517
5	6.38	0.00519	115	2.67	0.00532
10	6.17	0.00514	145	2 01	w
20	5.79	0.00496	180	1.40	0.00517
40	5.00	0.00516	240	0.42	0.00530
60	4.35	0.00507	300	−0.24	0.00531
80	3.71	0.00513	∞	−1.98	....

The best value of k as determined by plotting log $(\alpha - \alpha_\infty)$ against time is 0.00513.

tion (9) reduces to equation (1) so that the reaction appears to follow the unimolecular law, i.e., it is a first order reaction. Reactions of this type in which one of the reactants is used over and over again are called catalytic reactions; they will be discussed in more detail presently.

Determination of the Order of a Reaction. The question as to whether a reaction is unimolecular, bimolecular, or termolecular can be answered by substituting the data into the different formulas (6), (11), (17), and noting which gives a constant value of k throughout the course of the action.

The order of a reaction may be determined graphically by plotting different functions of the concentration c against the time, and determining which one of the following gives a straight line.

(1) log c vs. time gives a straight line for a unimolecular reaction.

(2) $1/c$ vs. time gives a straight line for a bimolecular reaction, in which $a = b$.

(3) $1/c^2$ vs. time gives a straight line for a termolecular reaction, in which $a = b = c$.

The order of a reaction may be determined also by observing the manner in which the period of half-life varies with the initial concentration.

(1) In a unimolecular reaction the time taken for a given fraction to react is independent of the initial concentration.

(2) In a bimolecular reaction the time taken for a given fraction to react is inversely proportional to the initial concentration, if $a = b$.

(3) In a termolecular reaction the time taken for a given fraction to react is inversely proportional to the square of the initial concentration, if $a = b = c$. These relations may be illustrated with data on the thermal decomposition of two different gases.

PH_3		N_2O	
Initial Pressure	Half-life	Initial Pressure	Half-life
707 mm.	84 sec.	296 mm.	255 sec.
79	84	139	470
37.5	83	52.5	860

The decomposition of phosphine is a first order reaction (but it is not unimolecular since it is catalyzed by the walls of the vessel), and the decomposition of nitrous oxide is bimolecular.

The period of half-life in a unimolecular reaction is $\ln 2/k$. The period of half-life in a bimolecular reaction, on the other hand, is $1/ka$, where a is the initial concentration. When different molecules are involved, the course of the reaction may be studied by altering the ratio of the reacting materials. For example, the oxidation of nitric oxide

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

is accelerated more by increasing the concentration of nitric oxide than by increasing the concentration of oxygen. This fact is in accord with the equation

$$\frac{dc_{NO_2}}{dt} = kc^2_{2NO} \times c_{O_2}.$$

Often a complex reaction may be simplified and studied by adding a large excess of one or more of the reactants. The reactant in large excess does not change its concentration and the changes in concentration of the other reactants may be studied alone.

Again, much information may be gained in a complex reaction by doubling the concentration of the reactants, one at a time, and observing the change in the reaction rate over a short period of time, during which the change in composition is not over 10 per cent. Since

$$\frac{dx}{dt} = kc^a{}_A c^b{}_B c^c{}_C$$

where A, B, and C represent the different molecules reacting and a, b and c are the corresponding coefficients in the reaction, it is seen that a can be evaluated by doubling c_A and measuring $\Delta x/\Delta t$. Thus for short time intervals

$$\left(\frac{\Delta x}{\Delta t}\right)_{(2c_A)^a, c^b{}_B, c^c{}_C} \div \left(\frac{\Delta x}{\Delta t}\right)_{c^a{}_A, c^b{}_B, c^c{}_C} = 2^a$$

and in the same way b can be determined by doubling c_B.

$$\left(\frac{\Delta x}{\Delta t}\right)_{c^a_A,\,(2c_B)^b,\,c^c_C} \div \left(\frac{\Delta x}{\Delta t}\right)_{c^a_A,\,c^b_B,\,c^c_C} = 2^b.$$

Complex Reaction Velocities. The mathematical description of reaction rates thus far has been confined to a few standard types but it must not be imagined that all reactions are amenable to simple mathematical treatment. In fact, one of the chief requirements at present in the study of kinetics is the choice of sufficiently simple reactions. The majority of reactions do not agree with the unimolecular, bimolecular, or termolecular equations. Frequently a reaction will follow one of these equations at first and then will gradually drift away from it. Among the various complications are (1) counter reactions, (2) side reactions, (3) consecutive reactions. These disturbing causes will now be considered.

(1) *Counter Reactions.* In the chemical change represented by the equation

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

the speed of the direct reaction steadily diminishes, owing to the ever-increasing effect of the reverse or counter reaction. Ultimately, when about two-thirds of the acid and alcohol are decomposed, the velocities of the two reactions become equal and a condition of equilibrium results.

The simplest way to determine the specific reaction rate of the forward reaction is to measure the reaction rate at the beginning, before there is an opportunity to accumulate appreciable quantities of the products. As a matter of fact, reactions involving this counter effect are frequently avoided in theoretical studies in kinetics. It is possible, however, to correct for the reverse reaction if the equilibrium constant is known.

Starting with a mols of acetic acid and a mols of alcohol, for example, the rate of the forward reaction is given by the expression

$$\frac{dx}{dt} = k_1(a - x)^2, \tag{20}$$

where x represents the amount of acid and alcohol decomposed, or the amount of ester and water formed at the time t, and k_1 is the specific reaction rate of the forward reaction.

The rate of the reverse reaction is given by the expression

$$\frac{dx'}{dt} = k_2x^2, \tag{21}$$

where k_2 is the specific reaction rate at which the concentration of ester and water *decrease*.

The difference between the two rates gives the actually observed rate, $\frac{dX}{dt}$, and

$$\frac{dX}{dt} = \frac{dx}{dt} - \frac{dx'}{dt} = k_1(a - x)^2 - k_2x^2. \tag{22}$$

But from the definition of the equilibrium constant,

$$K = \frac{k_1}{k_2},$$

or

$$k_2 = \frac{k_1}{K}. \tag{23}$$

and

$$\frac{dX}{dt} = k_1(a - x)^2 - \frac{k_1}{K}x^2. \tag{24}$$

In the reaction between acetic acid and ethyl alcohol, at room temperature, K has the value 4.0, and equation (24) may be integrated and solved for k_1.

(2) *Side Reactions.* When the same substances are capable of reacting in more than one way, with the formation of different products, the several reactions proceed side by side. Thus, benzene and chlorine may react in two ways, as shown by the equations,

$$(1)\ C_6H_6 + Cl_2 = C_6H_5Cl + HCl,$$

and

$$(2)\ C_6H_6 + 3\ Cl_2 = C_6H_6Cl_6.$$

It is generally possible to regulate the conditions under which the substances react, so as to promote one reaction and retard the other.

(3) *Consecutive Reactions.* By consecutive reactions, we understand those reactions, in which the products of a certain initial chemical change react, either with each other, or with the original substances, to form new substances. Attention has already been called to the fact, that many of our common chemical equations really represent the summation of a number of consecutive reactions. If the system A is transformed into the system C, through an intermediate system B, then we shall have the two reactions,

$$(1)\quad A \rightarrow B,$$

and

$$(2)\cdot\ B \rightarrow C.$$

If reaction (1) should have a very much greater velocity than reaction (2), then, the measured velocity of the change from A to C, will be prac-

tically the same as that of the slower reaction (2). This fact has been illustrated by means of the following analogy, due to James Walker*: "The time occupied by the transmission of a telegraphic message depends both on the rate of transmission along the conducting wire, and on the rate of progress of the messenger who delivers the telegram; but, it is obviously this last slower rate, that is of really practical importance in determining the time of transmission."

The saponification of ethyl succinate may be taken as an illustration of consecutive reactions. This reaction proceeds in two stages as follows:

(1) $C_2H_4\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} + NaOH \rightleftarrows C_2H_4\begin{matrix}COOC_2H_5\\COONa\end{matrix} + C_2H_5OH$

(2) $C_2H_4\begin{matrix}COOC_2H_5\\COONa\end{matrix} + NaOH \rightleftarrows C_2H_4\begin{matrix}COONa\\COONa\end{matrix} + C_2H_5OH$

In this case, the product of the first reaction reacts with one of the original substances.

Consecutive reactions are very common. In fact the equations as ordinarily written give little idea of the intermediate steps, and yet one of these intermediate steps may be the slowest reaction, i.e., the rate-determining reaction. Kinetic measurements offer one of the best methods for studying intermediate steps in a reaction.

For example, the reaction represented by the equation

$$2\,PH_3 + 4\,O_2 \rightarrow P_2O_5 + 3\,H_2O$$

involves six molecules of the reactants, but experiments show that the reaction is bimolecular, the velocity of the reaction being directly proportional to the concentration of the phosphine and to the concentration of the oxygen. On allowing the gases to mix slowly by diffusion it was discovered that the reaction actually takes place in several successive stages, the first stage being represented by the equation of the bimolecular reaction

$$PH_3 + O_2 \rightarrow HPO_2 + H_2.$$

The subsequent changes, involving the oxidation of the products of this reaction, take place with great rapidity.

Simple reactions, like the oxidation of hydrocarbons to give carbon dioxide and water, really pass through a series of intermediate stages involving the production of peroxides, alcohols, ketones, and acids.

It should be emphasized again that bimolecular reactions are by far

* Proc. Roy. Soc., Edinburgh, **22** (1898).

the most common type of reaction, that termolecular reactions are very rare because three-body collisions are much less probable than two-body collisions, and that higher orders do not need even to be considered. If more than three molecules appear to be involved in a reaction, it is practically certain that the reaction takes place in consecutive steps — most likely bimolecular steps.

Influence of Temperature. It has long been known as an empirical fact that many reactions approximately double or treble their velocity for a 10° rise.

A more quantitative relation, proposed by Arrhenius, is given in the following equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}, \tag{25}$$

in which k is the specific reaction rate, E is a constant, R is the gas constant, and T is the absolute temperature.

Integrating equation (25), we have

$$\log k = -\frac{E}{2.303 \times R}\frac{1}{T} + C, \tag{26}$$

or integrating between limits, T_2 and T_1,

$$\log \frac{k_2}{k_1} = \frac{E}{2.303 \times R}\left(\frac{T_2 - T_1}{T_2 T_1}\right). \tag{27}$$

It will be noted that these equations are like those for equilibrium constants studied on p. 283. According to equation (26), a straight line is produced when the logarithm of the specific reaction rate is plotted against the reciprocal of the absolute temperature. The specific decomposition rates of gaseous nitrogen pentoxide* at different temperatures are given in the second column of the following table, and they are shown graphically in Fig. 114.

THE DECOMPOSITION OF NITROGEN PENTOXIDE AT DIFFERENT TEMPERATURES

t° C.	$1/T$	$k_{obs.} \times 10^5$	log k	$k_{calc.} \times 10^5$	Half-life
65	0.002959	487	−2.313	477	2.38 min.
55	0.003048	150	−2.824	155	7.72 min.
45	0.003145	49.8	−3.303	47.2	21.8 min.
35	0.003247	13.5	−3.871	13 2	85.9 min.
25	0.003357	3.46	−4.471	3.46	5.71 hours
0	0.003663	0.0787	−6.104	0.0733	10.2 days

* Daniels and Johnston, J. Am. Chem. Soc., **43**, 53 (1921).

The slope of the line in Fig. 114 is -5400 and E has the value of 24,700. Equation (26) becomes

$$\log k = -\frac{24{,}700}{2.303 \times 1.98}\frac{1}{T} + 13.639. \qquad (28)$$

Using this formula, the calculated specific reaction rates are given in the fifth column of the table. The periods of half-life, calculated from the data in the third column are given in the last column.

The marked influence of temperature on reaction rates is clearly brought out in this table. Extrapolated values based on equation (28)

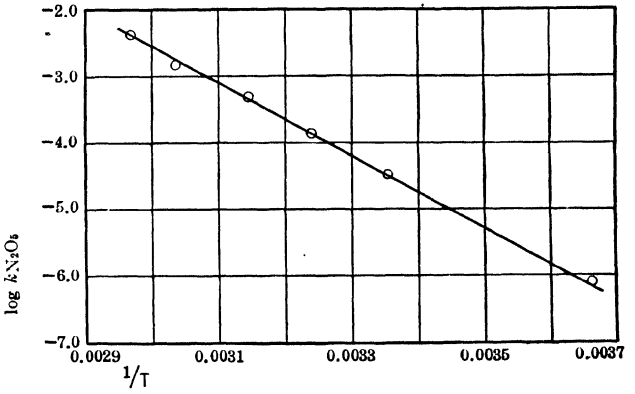


FIG. 114

are shown in the following table.

EXTRAPOLATED VALUES OF HALF-LIFE

$t°$ C.	Half-life	$t°$ C.	Half-life
300	0.000039 sec.	25	5.7 hours
200	0.0039	0	11 days
150	0.088	− 25	3 years
125	0.56	− 50	830 years
100	4.6	− 75	940,000 years
75	51.	−100	8.4 billion years

It should be emphasized that the range between reactions which are too slow to measure and those which are too fast to measure is really quite narrow.

Active and Passive Molecules. According to present theories, it is necessary for molecules to become activated before they can react. If all molecules were equally reactive, it would be difficult to account for

the very existence of slow reactions. Since the number of collisions per second is enormous, it might be expected that all reactions would be instantaneous. Ionic reactions, such as neutralizations and precipitations, are in fact immeasurably fast, but the ionic state may be regarded as an activated state.

The concept of activated molecules in kinetics goes back to Arrhenius. It is probable that he considered activated molecules as chemical individuals similar to isomers, but they are now regarded merely as molecules having higher energy contents, i.e., molecules with displaced electrons.

Energy of Activation. It will be noted that the empirical constant E of the Arrhenius equation (27) has the dimensions of energy since all the other factors reduce to pure numbers except RT. In all the recent developments in kinetics it is assumed that this constant E represents the energy required to activate a molecule so that it can react. The proof of equation (25) has its foundations in statistical mechanics.* It must be admitted that there are only a few direct experimental checks on this equation and that the development of kinetics through its use has not been as rapid as had been hoped for, but the equation and its significance have been generally accepted.

The close resemblance between this equation and the van't Hoff equation, which is thoroughly established, is indicated by the following:

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} \quad \text{and} \quad \frac{d \ln k_2}{dT} = \frac{E_2}{RT^2} \tag{29}$$

where k_1 refers to the specific rate of the forward reaction and k_2 to the specific rate of the reverse reaction.

Subtracting,

$$\frac{d(\ln k_1 - \ln k_2)}{dT} = \frac{E_1 - E_2}{RT^2} \tag{30}$$

$$\frac{k_1}{k_2} = K. \tag{31}$$

Assuming $E_1 - E_2 = q$,

$$\frac{d \ln K}{dT} = \frac{q}{RT^2}. \tag{32}$$

These relations are important, for they show that the heat of reaction measured in a calorimeter is equal to the difference between the energy required to activate the reactants and the energy required to activate the products. The situation may be clarified by reference to Fig. 115. The reacting molecules A require the absorption of a

* Tolman, J. Am. Chem. Soc., **47**, 1533 (1925).

definite quantity of energy E_1 to put them in an activated state B from which they can react to give the products C. The products themselves require the absorption of a certain quantity of energy E_2 in passing from C to B, and this same energy is evolved as heat in passing from B to C. Usually the heat evolved in the step BC is greater than that absorbed in the step AB, and the resultant effect is an evolution of heat corresponding to q. If E_1 happens to be greater than E_2, the reaction is endothermic.

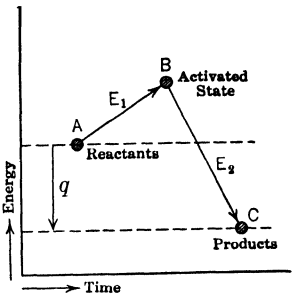


FIG. 115

Chemical equilibria and thermodynamics are concerned only with the initial and final states and with the resultant heat of reaction q, whereas chemical kinetics is concerned only with E_1 or E_2. The energy required for the activated state is the chief factor in determining the speed of the reaction. It will be shown in the following section that the greater the energy required for activation the fewer are the molecules possessing this energy and the slower is the reaction at a given temperature. It is clear that the heat of reaction q is of no significance for calculating reaction rates. As Hinshelwood has suggested, there is no more connection between the heat of reaction and the energy of activation than there is between the difference in levels of two valleys and the height of a mountain pass which separates them.

Kinetic Theory of Gases. Valuable information for studying reaction rates, concerning the distribution of energy among molecules and concerning the frequency of collisions, may be obtained from the kinetic theory of gases.

The unordered motion of colloid particles has been directly observed under the microscope, and we have every reason to believe that the motions of molecules in a gas are similar. A series of collisions in the right direction may give to a molecule an abnormally high velocity, and on the other hand a head-on collision may completely stop a molecule for a brief interval of time. Since the velocities are determined by chance, and since a large number of molecules is involved in any measurement, the laws of probability may be applied.

The law governing the distribution of velocities among molecules in a gas at constant temperature as first deduced by Maxwell is illustrated in Fig. 116. It will be observed that a large number of the molecules have nearly the same velocity and that the number of molecules having velocities greater or less than this most probable velocity becomes progressively less as the difference in velocity becomes greater. The

diagram gives the distribution curves at the temperatures 273° and 373° K. The number of molecules having abnormally high velocities shows the greatest proportional increase.

The derivation of Maxwell's distribution law is beyond the scope of this book.* An approximate form, which considers the distribution in

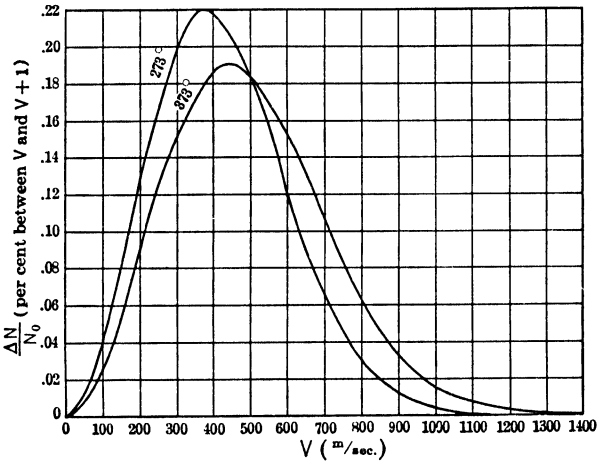


FIG. 116

two dimensions instead of three, leads to the following expression:

$$dn = n\frac{2}{a^2}e^{-\frac{c^2}{a^2}}c\,dc. \tag{33}$$

It is sufficiently accurate for most work in chemical kinetics. In this equation dn is the number of molecules having velocities between c and $c + dc$, and n is the total number of molecules. The most probable velocity is a and according to theorems in probability it is related to the root-mean-square velocity u as follows:

$$a^2 = \tfrac{2}{3}u^2. \tag{34}$$

It was shown in Chapter II that for a mol of gas

$$pv = RT = \tfrac{1}{3}mNu^2 \tag{35}$$

where N is the number of molecules in a mol.

Combining (34) and (35),

$$a^2 = \frac{2RT}{mN}. \tag{36}$$

* A simplified presentation is given by Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," pp. 6–13.

The kinetic energy E of N molecules (1 mol) moving with velocity c is given by the equation

$$E = \tfrac{1}{2} mNc^2, \quad \text{or} \quad c^2 = 2E/mN. \tag{37}$$

Combining (36) and (37),

$$\frac{c^2}{a^2} = \frac{E}{RT}. \tag{38}$$

Differentiating equation (37)

$$dE = mNc\, dc. \tag{39}$$

Substituting equations (36), (38) and (39) into equation (33)

$$dn = n \frac{1}{RT} e^{-E/RT}\, dE. \tag{40}$$

Integrating (40) between E and ∞,

$$\int_{n_E}^{n_\infty} dn = \frac{n}{RT} \int_E^\infty e^{-E/RT}\, dE = n \left[-e^{-E/RT} \right]_E^\infty. \tag{41}$$

The integral at the left represents the total number of molecules having energies equal to or greater than E, and may be represented by n'. Then

$$\frac{n'}{n} = e^{-E/RT}. \tag{42}$$

This important equation states that the *fraction* of the molecules in any group of molecules which have kinetic energies equal to or greater than E, is equal to the fraction, $e^{-E/RT}$. It is used in chemical kinetics to determine the number of activated molecules, and it is a special case of a statistical equation which finds wide applications in physics and chemistry, known as the Boltzmann equation.

Equation (42) may be illustrated by applying it to definite data. At 25° C., the fraction of molecules having a kinetic energy greater than 24,700 calories per mol is

$$e^{-\frac{24{,}700}{1.987 \times 298.1}} = 7.748 \times 10^{-19},$$

and at 35° C. it is

$$e^{-\frac{24{,}700}{1.987 \times 308.1}} = 3.003 \times 10^{-18}.$$

It is apparent that an increase of 10° in the neighborhood of room temperature has more than trebled the number of molecules having an energy greater than 24,700 calories per mol. The total kinetic energy PV of a mol of gas has increased by only 3.3 per cent, however, since $PV = RT$ and T has increased from 298 to 308. This enormous

increase in the number of molecules of high energy content is in agreement with Fig. 116 and with the large temperature coefficient of chemical reaction rates.

Molecular Collisions in Gases. Four quantities of use in chemical kinetics may be calculated from the kinetic theory of gases introduced in Chapter II. They are (1) number of molecules striking a surface, (2) the number of collisions per second between molecules in a gas, (3) the molecular diameters and (4) the distance a molecule can travel before it suffers a collision.

(1) *Number of Molecules Striking a Surface.* If n molecules are contained in a cube 1 centimeter on an edge, it may be assumed that one-sixth of them are moving toward one wall. The root-mean-square velocity is u centimeters per second, and the number of molecules hitting the wall in a second will be equal to one-sixth of the number which are within a distance of u centimeters from it. Even if one of these molecules is prevented from hitting the wall by colliding with another molecule, the second molecule will be deflected back so that the number of hits is the same. If there are n molecules in the 1-centimeter cube, the number hitting one wall (1 square centimeter) is $\frac{1}{6}nu$ (1^2). A closer analysis based on the unequal speeds of different molecules shows that the factor $\frac{1}{6}$ should be replaced by $\frac{3}{8}$. Then

$$\text{Collisions per square centimeter of wall per second} = \tfrac{3}{8}nu. \quad (43)$$

It was shown in Chapter II that the root-mean-square velocity u can be calculated from the density d of the gas and the pressure p by the following equation

$$u = \sqrt{\frac{3pv}{mn}} = \sqrt{\frac{3p}{d}}. \quad (44)$$

A simpler form for calculation is obtained for molar quantities by substituting the molecular weight M for mn and RT for pv,

$$u = \sqrt{\frac{3RT}{M}}. \quad (45)$$

Since u is expressed in centimeters per second, p must be expressed in dynes and R in ergs per degree.

(2) *Frequency of Collisions.* A rough idea of the number of collisions between molecules may be obtained from the following considerations. If the diameter of a molecule is σ and two molecules are just touching, the distance separating their centers is also σ. Considering molecules to be points, each molecule can collide with all other molecules which come within the distance σ from its center. A molecule moving with

velocity u centimeters per second will sweep out during a second a cylindrical space u centimeters long with an *effective* cross section $\pi\sigma^2$. The cylindrical space may be zigzag in shape on account of deflections suffered during collisions. If there are n molecules per cubic centimeter, this molecule will collide with $(u\pi\sigma^2)n$ other molecules. But each of the n molecules will sweep out this effective volume and undergo the same number of collisions. The total number of molecules undergoing collisions is therefore $(u\pi\sigma^2 n)n$. Certain approximations are involved in this derivation, and when corrections are made for the distribution of velocities and other factors, the number of molecules colliding becomes

$$\sqrt{2}\, u\pi\sigma^2 n^2.$$

The number of collisions is one-half the number of molecules colliding because two molecules are necessary for a collision. The number of collisions z per second per cubic centimeter is given by the equation

$$z = \tfrac{1}{2}\sqrt{2}\,\pi u\sigma^2 n^2. \tag{46}$$

Substituting for u its equivalent given in (45), combining and rounding off numbers, the following approximate equation is obtained:

$$z = 3.9\,\sigma^2 n^2 \sqrt{\frac{RT}{M}}. \tag{47}$$

(3) *Molecular Diameters.* All the quantities necessary for calculating the frequency of collisions are readily obtainable, except the molecular diameter σ. This quantity can be calculated from the viscosity measurements, similar to those described for liquids on p. 57. Many gases have been measured by Rankine,* and the following table of molecular diameters is based in part on his results.

MOLECULAR DIAMETERS (σ)

Gas	σ	Gas	σ
Helium	2.18×10^{-8} cm.	Hydrochloric acid	2.86×10^{-8} cm.
Argon	3.36	Hydrobromic acid	3.16
Chlorine	4.96	Hydriodic acid	3.50
Bromine	3.42	Carbon dioxide	4.18
Iodine	3.96	Hydrogen	2.47
Oxygen	3.39	Nitrogen pentoxide	8.53

Many of the diameters calculated from viscosity measurements are in close agreement with the diameters as calculated from X-ray measurements on crystals, and there is good evidence that the di-

* Proc. Roy. Soc., **91**, 201 (1915), and earlier papers. Phil. Mag., **29**, 552 (1915).

ameters of most molecules are of the order of 10^{-8} centimeters or about 1 Ångström unit. In fact, when there are no data available, it may be assumed for the purpose of estimating the number of collisions that the molecular diameter is 10^{-8} centimeters. In certain phenomena involving radiation, however, molecules appear to have effective diameters which are much larger.

(4) *Mean Free Path.* If a molecule travels u centimeters in a second and collides with $\sqrt{2}\, u\pi\sigma^2 n$ molecules per second as shown before, the average distance between encounters l, called the mean free path, is given by the equation

$$l = \frac{u}{\sqrt{2}\, u\pi\sigma^2 n} = \frac{1}{\sqrt{2}\, \pi\sigma^2 n}. \tag{48}$$

A knowledge of the mean free path is useful in calculations involving collisions with the walls of containing vessels, and rates of diffusion of gases.

Mechanism of Bimolecular Reactions. Equation (26) may be thrown into the exponential form, giving

$$k = se^{-E/RT}. \tag{49}$$

Here k is the specific reaction rate and $e^{-E/RT}$ is a numerical factor which represents the fraction of the molecules having energy equal to or greater than the activation energy E. As usual, R and T, signify the gas constant and the absolute temperature and s is a constant having the same dimensions as k.

The physical significance of the constant s becomes a matter of considerable importance. In bimolecular reactions it turns out that s is the number of molecules colliding. The rate of reaction then is equal to the number of molecules colliding multiplied by the fraction of the molecules which have energy as great as or greater than E. In other words, *reaction occurs in bimolecular reactions when activated molecules collide.* It is assumed that all the energy of a collision may go to one molecule.

This relationship may be checked with experimental data, as shown first by W. C. McC. Lewis. The decomposition of gaseous hydriodic acid has been found to be a bimolecular reaction at 283° C. with a specific reaction rate k of 3.5×10^{-7} sec.$^{-1}$, when the concentrations are expressed in mols per liter.

From the temperature coefficient of the rate of decomposition the value of E has been found by equation (27) to be 44,000 calories. Then the fraction of molecules in the activated state $= e^{-E/RT} = e^{\frac{-44{,}000}{1.9885 \times 556}} = 5.199 \times 10^{-18}$. The number of molecules colliding, s,

is twice the number of collisions as given by equation (46). u is calculated by equation (45) to be 3.3×10^4 cm. per sec. The diameter σ has been found from viscosity measurements to be 3.5×10^{-8} cm. If the concentration of hydriodic acid is 1 mol per liter, the concentration n per cubic centimeter is $6.06 \times 10^{23}/1000$, or 6.06×10^{20}. Then

$$s = 2z = \sqrt{2}\,\pi\sigma^2 u n^2 = \sqrt{2} \times 3.14 \times (3.5 \times 10^{-8})^2 \times 3.3 \times 10^4 \times (6.06 \times 10^{20})^2 = 6.593 \times 10^{31}.$$

Dividing by Avogadro's number and multiplying by 1000 to express the collisions in terms of mols colliding per second per liter,

$$s = \frac{6.593 \times 1000 \times 10^{31}}{6.06 \times 10^{23}} = 1.088 \times 10^{11}.$$

Then substituting into equation (49), we have

$$k = se^{-E/RT} = 1.088 \times 10^{11} \times 5.199 \times 10^{-18} = 5.66 \times 10^{-7}.$$

The agreement with the experimentally determined value, 3.5×10^{-7}, is very good considering the uncertainties involved in some of the constants and the large influence of a small error in the value of E.

This calculation is given at length because it illustrates one of the few types of reactions where the velocity can now be predicted theoretically from independent data.

The Significance of the Temperature Coefficient. It has been stated that most reactions at room temperature double or treble their speed for a 10° rise in temperature. This is a fundamental generalization which finds important applications in practical chemistry, in the growth of bacteria and in many natural processes. Reactions produced by light are exceptions to this rule as explained in a later chapter.

The existence of the universal temperature coefficient may be explained in part with the help of equations (49) and (27):

$$k = se^{-E/RT}$$

$$\log \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{2.303 \times 1.987 \times T_2 T_1}.$$

At room temperature E/RT usually has a numerical value in the neighborhood of 40 and s changes only slightly with temperature. The form of the exponential equation (49) is such that changing k ten thousand-fold or a hundred thousand-fold changes E by only a few per cent. But our rate measurements are usually limited to this

range because it is difficult to measure reactions which are completed in much less than a minute and we do not ordinarily have the patience to measure reactions which continue over a month.

If E varies by only a few per cent, $\log k_2/k_1$ must vary by only a few per cent and the ratio of k at two temperatures (10° apart for example) is, therefore, nearly the same for all reactions whose reaction rates are convenient to measure.

This relation is supported by the fact that reactions of a similar nature may vary widely in absolute velocities but they have very nearly the same temperature coefficients.*

The Mechanism of Unimolecular Reactions. In bimolecular reactions it has been shown that s in equation (49) may be interpreted as representing the number of collisions. In unimolecular reactions such an interpretation leads to calculations which are not at all in agreement with experimental facts. It is possible that in unimolecular reactions s is the frequency not of collision but of oscillation of atoms in the molecule.

At first sight a unimolecular reaction appears to be entirely independent of collisions. For example, it may be imagined that a certain number of gas molecules are decomposing in a cylinder and that the volume is suddenly doubled. The pressure is halved and the number of collisions is one-quarter as great as it was before; but experimental facts show that the fraction decomposing per second is just the same in a unimolecular reaction as it was before, at the higher pressure. The fact that the reaction rate appears to be independent of collision frequency led to the invention of the radiation hypothesis, according to which it was supposed that the molecules in a unimolecular reaction receive their energy of activation from radiation emitted by the walls of the containing vessel. This hypothesis has been disproved by experimental tests,† and it is now apparent that molecules in a unimolecular reaction receive their energy of activation from collisions. However, there is a time lag between activation and decomposition and during this interval of time many activated molecules become deactivated by collisions. The direct relation between collision and decomposition is accordingly lost. In support of this explanation there is evidence that at very low pressures unimolecular reaction rates fall off and become bimolecular. At sufficiently low pressures the time between collisions may be made large compared to the time lag between activation and decomposition, and under these conditions

* Specific Calculations illustrating these relations are given in J. Am. Chem. Soc., **52**, 1472 (1930).

Daniels, Chem. Rev., **5**, 39 (1928).

the decomposition rate depends on the collision frequency, i.e., the reaction is bimolecular.

Unimolecular reactions are found chiefly among complex molecules with many atoms, for in these a longer time may be required before the energy of activation generated by collisions becomes localized in the particular bond which is about to be ruptured. Simple molecules are not apt to decompose in a unimolecular manner if the products contain free atoms, because the energy required to produce free atoms is so large.

The following table gives a few unimolecular reactions; it will be noticed that all involve complex molecules.

	Temperature at which $k = 1.7 \times 10^{-3}$	Energy of Activation
N_2O_5	328° K.	24,700
$C_3H_7N=NC_3H_7$	545	40,900
$CH_3N=NCH_3$	599	51,200
CH_3OCH_3	800	58,500
C_2H_5CHO	785	54,000

Catalysis. It is a familiar fact that the velocity of a chemical reaction is frequently accelerated by the presence of a foreign substance which remains unchanged when the reaction is complete. For example, cane sugar is inverted very slowly by pure water alone, but when a trace of acid is added, the rate of inversion is greatly increased. A substance which is capable of exerting such an accelerating action is termed a *catalyst* and the process is known as *catalysis*. A catalyst has been defined by Ostwald as "an agent which affects the velocity of a chemical reaction without appearing in the final products of the reaction."

A catalyst is powerless to change the equilibrium; it simply hastens the rate of attainment of equilibrium. It is obvious that the catalyst must accelerate the reverse reaction to the same extent as the forward reaction so that their ratio, the equilibrium constant, is unaffected.

Sometimes the catalyst may appear to change the equilibrium but in such cases large quantities of the catalyst are usually required and the material not only accelerates the reaction but it also changes the activities or effective concentrations of the reacting materials. Changing the solvent, for example, may accelerate a reaction, and it may also

change the equilibrium, but the two effects are entirely independent. The catalytic effect is not responsible for the equilibrium shift.

The function of the catalyst is to bring about the desired reaction with a smaller energy of activation. A lower energy of activation gives a more rapid reaction because more molecules have the necessary amount of energy to react. Referring to Fig. 115, it will be seen that the finding of a catalyst is analogous to finding a lower route than the one represented by B, in passing from A to C. The high energy requirement is avoided by some by-pass. Usually the by-passing consists in forming a new compound with less energy consumption and then decomposing this intermediate compound in such a way as to regenerate the catalyst. In this way the catalyst is used over and over again.

Thus if a reaction represented by the equation

$$A + G = AG,$$

takes place very slowly under ordinary conditions, it is possible to accelerate its velocity by the addition of an appropriate catalyst H. Then

$$(1)\ A + H = AH.$$
$$(2)\ AH + G = AG + H.$$

The catalytic action of nitrogen dioxide in the oxidation of sulphur dioxide offers a good example. The rate of the reaction represented by the equation

$$2\,SO_2 + O_2 = 2\,SO_3$$

is very slow. The accelerating action of nitric oxide on the reaction may be represented in the following simplified manner:

$$(1)\ 2\,NO + O_2 = 2\,NO_2.$$
$$(2)\ 2\,SO_2 + 2\,NO_2 = 2\,SO_3 + 2\,NO.$$
$$(3)\ 2\,NO + O_2 = 2\,NO_2, \text{ etc.}$$

Numerous examples in support of the intermediate compound theory of catalysis are found in the realm of organic chemistry. Probably the most familiar is the preparation of ether from alcohol using sulphuric acid as the catalyst. That an intermediate compound is actually formed in this reaction was first proved by Williamson, who detected the presence of ethyl sulphuric acid in the reaction mixture. The catalytic action of aluminum chloride in the well-known Friedel-Crafts synthesis of organic compounds has been shown to be due to the formation of an addition compound.

Kendall has shown through freezing-point-composition curves that addition compounds are formed between the acid and base in many reactions which give esters. In fact the phenomenon of catalysis through intermediate compound formation is so general that many chemists believe that nearly all organic reactions are preceded by *addition*, followed by rearrangement or dissociation.

It must be emphasized that the conditions for catalysis are rather specific. If the intermediate compound is too stable, no further decomposition is possible. It must have just the right degree of stability.

If the formation of intermediate compounds is interpreted broadly to include loose compounds of a physical nature, such as adsorption at a surface, or transitory cohesions between molecules, the theory may be made quite general.

Sometimes one of the products of reaction functions as a catalyst and, for a while, the reaction increases in velocity. Such a substance is called an *auto-catalyst.* Normally, of course, the reaction rate decreases continually but in auto-catalytic reactions the rate increases to a maximum and then decreases.

Contact Catalysis.* The phenomenon of adsorption has been described and it was suggested that in many cases the surface of a solid may be regarded as a checkerboard of atoms on which molecules from the gas phase, or from solution, may become attached. The adsorbed layer is then limited to a thickness of one molecule. There may be further condensation of easily liquefiable gases in the minute capillaries of substances like charcoal and silica gel, but this phenomenon is not ordinarily involved in catalysis.

When molecules are adsorbed at a surface the energy content is altered and there is opportunity for forming new products. Adsorption does not necessarily produce catalytic reactions but catalytic reactions at surfaces generally involve adsorption.

The rate of a reaction catalyzed by a surface depends to a large extent on the fraction of the surface which is covered with adsorbed gas. When the surface is nearly bare the pressure of the gas determines the extent of adsorption, and this in turn determines the speed of the reaction. Since the reaction rate is proportional to the concentration

* This subject has been intensively and helpfully described through the annual reports of the committee on Contact Catalysis of the National Research Council beginning in 1924. The reports have been published in Industrial Engineering Chemistry and in the Journal of Physical Chemistry. They may be obtained from the National Research Council. Taylor has given an excellent treatment of the subject in his " Treatise on Physical Chemistry," second edition.

of the gas, the reaction follows the unimolecular equation, i.e., it is a reaction of the first order. When the surface is practically saturated, on the other hand, the pressure of the gas has no influence on the reaction rate and the reaction is of the "zero order." When ammonia is decomposed on a tungsten filament, for example, the rate of decomposition is independent of the pressure, over a wide range of pressure.*

When the surface is partly covered, the reaction rate is proportional to p^n where p is the pressure and n is some fractional number which is determined empirically by experiment.

It is likely that contact catalysis does not involve all the atoms at the surface but that it is concerned with a small portion which happens to be specially unsaturated or particularly rich in energy.

The activity of a catalyst is appreciably altered by extremely minute amounts of foreign substances. Foreign substances which tend to inhibit catalytic activity are known as *poisons*; substances which tend to enhance the activity are known as *promoters*. It is easy to see how a small number of molecules can react permanently with the surface atoms to destroy the catalyst. For example, in the manufacture of sulphuric acid by the contact process, the presence of a very minute amount of arsenic completely destroys the catalytic activity of the platinum catalyst by forming platinum arsenide at the surface. Certain metals and metallic oxides act as promoters in some cases by rendering the catalyst less susceptible to poisoning, but in many cases they act by permitting loose adsorption compounds which have just the right degree of stability to produce a rapid catalytic reaction. In the Haber process for the synthesis of ammonia with an iron catalyst, for example, the addition of a trace of certain metals such as vanadium produces a large increase in catalytic activity.

The catalytic activity of the walls of the containing vessel is a factor in many gaseous reactions. The thermal decomposition of organic materials frequently occurs on the walls. In such cases the temperature coefficient is usually small because the slowest process is the diffusion of the products away from the walls and a diffusion process is subject only to the simple laws of the kinetic theory of gases. A 10° rise at about 300° K. increases the diffusion rate only about 3 per cent, whereas a chemical reaction is normally increased about 300 per cent, as already explained. If the slowest step is the adsorption process, the temperature coefficient may be high, however, because such an adsorption is a type of chemical reaction. A wall effect may be distinguished from a homogeneous gas reaction by (1) the temperature coefficient; (2) increasing the area greatly, as by adding powdered

* Hinshelwood and Burk, J. Chem. Soc., **127**, 1552 (1925).

glass to a glass vessel; (3) changing the nature of the vessel walls. Quartz may be used instead of glass, for example, or the walls may be coated. The reaction between bromine and ethylene is a wall effect, as shown by the fact that the reaction is completely stopped when the glass walls are covered with paraffine.*

Some Applications of Catalysis. A few of the many applications of catalysis in the realm of industrial chemistry should be briefly mentioned.

(1) *The Haber Process.* By a careful study of the conditions governing the equilibrium represented by the equation,

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3,$$

and by the employment of proper catalytic agents, Haber succeeded in producing ammonia on a commercial scale by means of this reaction. The synthesis of ammonia is now one of the large chemical industries both in this country and abroad. At 1000°, ammonia may be regarded as completely dissociated, while at 550°, and under atmospheric pressure, only about 0.08 per cent of ammonia is formed. Increase of pressure, however, displaces the equilibrium, in accordance with the principle of Le Chatelier, so that more of the system occupying the smaller volume, namely ammonia, is formed. Thus, at 550°, and under a pressure of 200 atmospheres, the amount of ammonia formed is nearly 12 per cent. Despite the fact that this percentage is so small, this amount of ammonia can be removed as ammonia of crystallization by ammonium nitrate, at a low temperature, and fresh portions of hydrogen and nitrogen introduced into the reaction chamber, thus rendering the process continuous. Various catalysts have been employed, including pure iron and alloys of iron. With this catalyst and suitable promoters, it is claimed that the process can be conducted efficiently at pressures as low as 50 atmospheres. Here, again, the catalyst is very susceptible to the presence of poisons such as sulphur, selenium, tellurium, arsenic, etc. It is stated that 0.01 per cent of sulphur is sufficient to destroy completely the catalytic activity of the iron catalyst.

(2) *Sabatier's Hydrogenation Process.* Toward the latter part of the nineteenth century, Sabatier and Senderens† discovered that reduced nickel will bring about the combination of hydrogen with ethylene, or acetylene, with the formation of ethane, as shown by the equations,

$$C_2H_4 + H_2 = C_2H_6,$$
$$C_2H_2 + 2\ H_2 = C_2H_6.$$

* Norrish and Jones. J. Chem. Soc., 55 (1926).

† Compt. rend., **124**, 1358 (1897); **128**, 1173 (1899).

In this method of hydrogenation, the vapor of the substance to be reduced is mixed with hydrogen and passed over a specific catalyst, which is maintained at a temperature ranging from 150° to 300°. The process is extremely rapid, and furthermore it requires a minimum amount of attention. The yields are relatively high, provided proper care is taken to maintain the temperature within the prescribed limits necessary to minimize the formation of secondary products. Although nickel is the most efficient catalyst, other metals, such as cobalt, platinum, iron and copper, may be used. It is absolutely essential that great care be taken in the preparation of the catalyst since the success of the method is largely dependent upon the condition of the metal. The catalyst is very susceptible to various poisons, particularly chlorine, sulphur, arsenic and phosphorus, and their compounds.

The process has found numerous applications, notably in the preparation of artificial perfumes. It also has proved of value in the synthesis of cyclohexanol and *p*-methylcyclohexanol, from phenol and *p*-cresol, respectively. Both of these substances are used in the preparation of isoprene and butadiene, compounds of importance in connection with the synthesis of artificial rubber. Undoubtedly the most important industrial application of the hydrogenation process is in the conversion of unsaturated aliphatic acids, such as oleic acid, into saturated acids, such as stearic acid.

(3) *Sabatier's Dehydrogenation Process.* Sabatier and his associates also showed that, at a given temperature, either water, or hydrogen, may be split off from alcohols, depending upon the nature of the catalyst employed. Such finely divided metals as copper, cobalt, nickel, iron, platinum and palladium, together with such anhydrous oxides as the lower oxides of manganese, tin, uranium, molybdenum and vanadium, have been found to function as catalysts in the dehydrogenation process. The dehydrogenation of both primary and secondary alcohols is most readily brought about by the use of reduced copper as a catalyst. On passing an aliphatic alcohol over the latter, at a temperature of 200° to 300°, a yield of fully 50 per cent aldehyde, or ketone, may reasonably be expected.

The chief technical application of this process is to the production of formaldehyde from methyl alcohol. In this process, air is drawn through methyl alcohol, maintained at a temperature suitable for saturation, and the mixture is then passed into a reaction chamber, over copper gauze, as a catalyst. The reaction which occurs may be represented by the equations,

$$2\,CH_3OH + O_2 = 2\,HCHO + 4\,H + O_2 = 2\,HCHO + 2\,H_2O.$$

(4) *Removal of Carbon Monoxide from the Air.* The presence of varying amounts of carbon monoxide in the air, due to the incomplete combustion of solid and liquid fuels, together with its presence in the products of combustion of smokeless powder, renders the development of adequate means for its elimination of the utmost importance. It is particularly hazardous in garages. A method for its elimination was successfully devised by Lamb, Bray and Frazer.* After much experimentation, it was found that when a mixture of air and carbon monoxide is passed, at ordinary temperatures, over a catalyst consisting of 50 per cent MnO_2, 30 per cent CuO, 15 per cent Co_2O_3, and 5 per cent Ag_2O, the carbon monoxide is completely oxidized to carbon dioxide. This catalytic mixture, called "hopcalite" by its discoverers, has been shown to be capable of acting indefinitely against any concentration of carbon monoxide, provided the air is dry.

(5) *The Welsbach Mantle.* The ignited Welsbach incandescent gas mantle consists of a fragile web of the oxides of thorium and cerium. Pure thoria gives relatively little light, but if progressive amounts of ceria are added, the luminosity gradually increases and attains maximum brightness when 1 per cent of ceria has been added. It is believed that this increase in luminosity is due to the alternate oxidation and reduction of the ceria, as indicated by the equation,

$$O_2 + 2\ Ce_2O_3 \rightleftarrows 4\ CeO_2.$$

The presence of 1 per cent of ceria in the mixture is sufficient to insure maximum velocity of surface combustion.

(6) *Synthesis of Methanol.* One of the outstanding recent developments in industrial chemistry has been the large-scale production of methyl alcohol from carbon monoxide and hydrogen using a zinc oxide-chromium oxide mixture as a catalyst.† The reaction is easily controlled and the catalyst is permanent. Pressures up to 200 atmospheres and temperatures between 200° and 400° are ordinarily used. Some of the higher alcohols have been synthesized in a similar manner but it becomes increasingly difficult to suppress side reactions as we ascend in the series.

The Rôle of Ferments and Enzymes in Catalysis. It is apparent that catalysis is of great importance in connection with many industrial processes as well as in the field of pure chemistry. The majority of the reactions occurring within living organisms have likewise been found to be accelerated catalytically by unorganized ferments, or

* J. Ind. Eng. Chem., **12**, 213 (1920).

† Ind. Eng. Chem., **21**, 1052 (1929); **22**, 1037, 1040 (1930). A description of manufacture is given in Ind. Eng. Chem., **22**, 433 (1930).

enzymes. Thus, before the process of digestion can proceed, starch must be changed into sugar. This transformation is accelerated by an enzyme called *ptyalin* occurring in the saliva, and by other enzymes found in the pancreatic juice. The digestion of albumin is hastened by the enzymes, *pepsin* and *trypsin*. As a rule, each enzyme acts catalytically on just one reaction or, in other words, the catalytic action of enzymes is specific. Enzymes are very sensitive to traces of certain toxic substances such as hydrocyanic acid, iodine, and mercuric chloride.

Catalytic Reactions in Solution. It has already been shown in this chapter that acids and bases act as catalysts for the inversion of cane sugar, the hydrolysis of esters and many other reactions. The most fruitful explanation is that of Brönsted,* according to which a complex is formed between the reactant and the acid (or base) in agreement with the general intermediate-compound theory of catalysis. The slowest or rate-determining step is the transfer of the hydrogen atom, or proton, from the acid to the reactant, within the complex molecule. After this rearrangement the complex molecule breaks down rapidly, yielding a molecule of the product and returning the proton to another molecule where it is used over again.

Other reactions are effected through a catalytic pair which is alternately oxidized and reduced. An example is the bromine-bromide catalysis of the hydrogen peroxide decomposition.† In acid solutions bromide ion is oxidized to hypobromous acid by hydrogen peroxide according to the equation

$$H_2O_2 + Br^- + H^+ = HBrO + H_2O,$$

and the hypobromous acid in turn is reduced by hydrogen peroxide according to the equation

$$H_2O_2 + HBrO = H_2O + Br^- + H^+ + O_2.$$

The second reaction is faster than the first but eventually a *steady state* is reached in which the concentrations of bromide ion, hypobromous acid, and hydrogen ion are constant and the only apparent change is

$$2\,H_2O_2 = 2\,H_2O + O_2.$$

Inert or "neutral" salts added to a reaction sometimes act as catalysts. It is believed that the reacting materials, A and B, unite to give a complex X which then decomposes into new products, M and

* Chem. Rev., **5**, 231 (1928).

† Bray and Livingston, J. Am. Chem. Soc., **45**, 1251 (1923).

N, according to the equation

$$A + B = X = M + N,$$

and that the effective concentration of X determines the rate of the reaction. This effective concentration of X may be markedly affected by the addition of foreign materials.

In the case of ionic reactions, the concentration of this complex, X, can be estimated, roughly, from the ionic strength, μ, of the solution, and the effects of different valence types predicted in this way agree with the experimental facts.* Sometimes a reaction which gives new ions as products may be rendered simpler to study by the simple artifice of adding a large excess of salt to the solution. The disturbing effect caused by the creation of more ions in the reaction itself is then minimized by the excess of ions already present and the reaction rate becomes more uniform.

Chain Reactions. In certain exothermic reactions the energy-rich molecules formed in the reaction collide with other molecules and activate them. After these activated molecules react, they are able, in turn, to activate more molecules and so a *chain* is formed. Sometimes, but not always, these activated products can be identified as definite chemical substances, and then it is possible to express the reaction of the chain with a stoichiometrical equation.† The chain theory was first proposed by Bodenstein and by Nernst to account for the large yield obtained in the photochemical combination of chlorine and hydrogen to give hydrochloric acid. The reaction appears to be as follows:

$$\begin{aligned} Cl_2 + \text{light} &= 2\,Cl \\ Cl + H_2 &= HCl + H \\ H + Cl_2 &= HCl + Cl \\ Cl + H_2 &= HCl + H, \text{ etc.} \end{aligned}$$

This cycle continues in some cases until over a million molecules have reacted. The chains can be started by other means than light; for example, by bombardment with alpha particles from radium, or by reaction with traces of sodium vapor, or by a spark.

One may ask why such a reaction ever stops. As a matter of fact the chain reaction does not stop in some cases until the material is consumed. Explosions, for example, are excellent examples of chain reactions. In many cases, however, the chain is broken when one of

* Further material on these subjects is given by Livingston, J. Chem. Education, **7**, 2887 (1930).

† Bodenstein, Chem. Rev., **7**, 215 (1930).

the activated molecules in the chain collides with the wall of the containing vessel or with foreign material which may be present as an impurity.

Certain oxidations in the gas phase have been successfully explained on the basis of chain reactions. The specific velocity of the reaction depends among other things on the size of the vessel, the pressure on the gases and the temperature. The various factors have been expressed mathematically by Semenoff* in studies on the oxidation of phosphorus vapor and sulphur vapor. If at any time the generation of heat in the reaction becomes greater than the rate at which the heat is dissipated to the vessel, the chains become infinite in length and an explosion is produced. The explosion is prevented if the energy is dissipated with sufficient rapidity by radiation to the walls, by collision with walls and inert molecules, or by collision with molecules which react chemically without perpetuating the chain. That the chains are stopped by colliding with the walls of the vessel can be shown in the oxidation of phosphorus by the fact that the explosion can be stopped by reducing the pressure. Under these conditions the mean free path is longer and the activated molecules reach the walls more often. The length of the chain is equal to the total number of molecules of product obtained, divided by the number of chains started, and it may be measured in some cases by photochemical means as described later in Chapter XX.

Certain foreign materials called *inhibitors* may retard a chain reaction greatly. If each molecule of the inhibitor stops a chain and each chain contains a great many molecules, it is obvious that mere traces of inhibitors are sufficient. For example, the oxidation of sodium sulphite by atmospheric oxidation is markedly inhibited by the addition of only a millionth of a mol of mannitol to a liter of solution.† Lead tetraethyl in gasoline is probably another example of an inhibitor. Under certain conditions the chain reactions become too violent in a combustion engine and a "carbon knock" is produced. A trace of the volatile lead compound, or possibly colloidal lead formed by its decomposition, is sufficient to stop the chains and prevent the knock.

In some reactions traces of water vapor, or grease from stop-cocks often act as inhibitors and shorten the chains.

The walls of the containing vessel do not always stop chains but sometimes they aid in initiating them. For example, in the decom-

* Chem. Rev., **6**, 347 (1929).

† Bigelow, Z. physik. Chem., **26**, 493 (1898). Young, J. Am. Chem. Soc., **24**, 297 (1902).

position of ozone in the presence of bromine, the chains are started by an unstable intermediate compound formed at the walls, and the reaction becomes explosive under certain conditions at room temperatures.*

REFERENCES

Kinetics of Chemical Change in Gaseous Systems. Hinshelwood.
Treatise on Physical Chemistry. Taylor. Chapters XIV and XV.
Catalysis in Theory and Practice. Rideal and Taylor.
Catalysis and Its Industrial Applications. Jobling.
Statistical Mechanics with Applications to Physics and Chemistry. Tolman.
Kinetics of Homogeneous Gas Reactions. Kassel.
Introduction to Statistical Mechanics for Students of Physical Chemistry. Rice.
Kinetics of Homogeneous Reactions. Chem. Rev. **10**, 1–264 (1932).
Chemical Statics and Dynamics. Mellor. Chapters II to VII and X and XI.

PROBLEMS

1. In a certain unimolecular reaction, half of the material is decomposed in 180 minutes:

(*a*) How long will it be until only one-tenth is left?

(*b*) How many minutes are required for the reaction to be 99 per cent completed?

(*c*) How much was left undecomposed at the end of the first half-hour?

2. Calculate x in the table on page 324.

3. From the following data show that the decomposition of H_2O_2 in aqueous solution is a unimolecular reaction:

Time in minutes	0	10	20
n	22.8	13.8	8.25 cc.

n is the number of cubic centimeters of potassium permanganate required to decompose a definite volume of the hydrogen peroxide solution.

4. When a solution of dibromsuccinic acid is heated, the acid decomposes into brom-maleic acid and hydrobromic acid according to the equation,

$$\begin{matrix} CHBr \cdot COOH \\ | \\ CHBr \cdot COOH \end{matrix} = \begin{matrix} CH \cdot COOH \\ \| \\ CBr \cdot COOH \end{matrix} + HBr.$$

After t minutes, the titre of a given volume of solution was x cc. of standard alkali.

t	0	214	380
x	10.09	10.37	10.57

(*a*) Calculate the velocity constant of the reaction.

(*b*) After what time is one-third of the dibromsuccinic acid decomposed?

5. Hinshelwood measured the decomposition rate of molten malonic acid

$$CH_2(COOH)_2 = CO_2 + CH_3COOH$$

by measuring the increase in pressure at constant volume. At 136.4° C. the pressure after 15 minutes was 53.0 mm.; after 56 minutes, 155.0 mm.; the final pressure was 302.0 mm. (*a*) Calculate the velocity constant and (*b*) determine the period of half-life. *Ans.* $t_{\frac{1}{2}} = 53.9$ min.

* B. Lewis and Feitknecht, J. Am. Chem. Soc. **53**, 2190 (1931).

6. Calculate y in the table on page 328.

7. Calculate z in the table on page 328.

8. In the saponification of ethyl acetate by sodium hydroxide at 10°, y cc. of 0.043 molar hydrochloric acid was required to neutralize 100 cc. of the reaction mixture, t minutes after the commencement of the reaction.

t	0	4.89	10.37	28.18	∞
y	61.95	50.59	42.40	29.35	14.92

Calculate the velocity constant, when the concentrations are expressed in mols per liter. *Ans.* $k_{\text{average}} = 2.38$.

9. Calculate w in the table on page 331.

10. Rideal and Thomas studied polarimetrically the racemization of potassium chromioxalate. The observed angles of rotation for a 0.00130 molar solution at 11° C. at times t are given in the table. Determine the velocity constant by the graphical method. The angle of rotation is the measure of the amount of material left.

$t_{\text{min.}}$	α	$t_{\text{min.}}$	α
5	0.460°	35	0.267°
10	0.420	40	0.245
15	0.385	50	0.205
20	0.351	60	0.171
25	0.320	70	0.143
30	0.292	80	0.123

11. Calculate the specific reaction rates k from the data in the table on page 332 for the dissociation of (*a*) phosphine and (*b*) nitrous oxide.

12. The velocity constant of formation of hydriodic acid from its elements is 0.00023; the equilibrium constant at the same temperature is 0.0157. What is the velocity constant of the reverse reaction? *Ans.* 0.0146.

13. The velocity constant k_c expressed in mols per liter, for the reaction

$$2\,NO + O_2 = 2\,NO_2$$

at 600° K. is 6.63×10^5; at 645° K. it is 6.52×10^5. For the reverse reaction, k_c is 83.9 and 407 at these two temperatures.

(*a*) Calculate the equilibrium constants at the two temperatures.

(*b*) Calculate ΔU for the reaction.

(*c*) Calculate ΔH. The experimentally determined value of ΔH is $-28{,}483$ cals.

14. Calculate from the data given the specific decomposition rate of nitrogen pentoxide and the period of half-life at $-10°$ C.

15. The velocity constants in the reaction represented by the equation

$$2\,AsH_3 = 2\,As + 3\,H_2,$$

are $k = 0.00035$ at 256° C., and $k = 0.0034$ at 367° C. Calculate the value of the velocity constant at 400° C.

16. Hinshelwood obtained velocity constants for the decomposition of molten malonic acid (problem 5) as follows:

t ° C.	125.9	129.4	133.6	134.2
k	0.00470	0.00643	0.00914	0.0105
t	142.3	143.5	153.6	
k	0.0218	0.0228	0.0661	

Plot log k against $1/T$, and find the energy of activation. *Ans.* 32,100 cal.

17. Oxygen is contained in a vessel at 1 atmosphere pressure at 25° C. Calculate,
(*a*) the number of collisions on the walls per sec. per sq. cm.
(*b*) the number of collisions between molecules per cc.
(*c*) the mean free path. *Ans.* (*a*) 2.7×10^{23}.

18. Oxygen is contained in a vessel at 1 mm. pressure and 25° C. Calculate,
(*a*) the number of collisions on the walls per sec. per sq. cm.
(*b*) the number of collisions between molecules per cc.
(*c*) the mean free path. *Ans.* (*b*) 1.3×10^{23}.

19. Oxygen is contained in a vessel at 1 atmosphere pressure and 500° C. Calculate,
(*a*) the number of collisions on the walls per sec. per sq. cm.
(*b*) the number of collisions between molecules per cc.
(*c*) the mean free path.

20. Hydrogen is contained in a vessel at 1 atmosphere pressure at 25° C. Calculate,
(*a*) the number of collisions on the walls per sec. per sq. cm.
(*b*) the number of collisions between molecules per cc.
(*c*) the mean free path.

21. The thermal decomposition of gaseous acetaldehyde is a bimolecular reaction. The value of E is 45,500 cal. per mol, and the molecular diameter of the acetaldehyde molecule is 5×10^{-8} cm. Calculate the number of molecules reacting per cc. per second at 800° K. and 760 mm. pressure, and compare with the observed value 7.3×10^{16}.

22. The chemical equation for the reaction between potassium oxalate and mercuric chloride is:

$$2\,HgCl_2 + K_2C_2O_4 = 2\,KCl + 2\,CO_2 + Hg_2Cl_2.$$

The weight of Hg_2Cl_2 precipitated from different solutions in given time, at 100° C., was as follows:

$HgCl_2$ (mols per liter)	$K_2C_2O_4$ (mols per liter)	Time (min.)	Mols of Hg_2Cl_2 precipitated
0.0836	0.404	65	0.0068
0.0836	0.202	120	0 0031
0.0418	0.404	60	0.0032

Write the differential equation for the reaction rate.

CHAPTER XV

ELECTRICAL CONDUCTANCE

Historical Introduction. Although the early observations of Beccaria and others pointed to the probability of the existence of some relation between chemical and electrical phenomena, it was not until the beginning of the nineteenth century that the science of electrochemistry had its birth. The epoch-making discovery, by Volta, of a means of obtaining electrical energy from chemical energy, gave the initial impulse to all the brilliant discoveries and investigations upon which the modern science of electrochemistry is based. The apparatus devised by Volta, known as the *voltaic pile*, consisted of discs of zinc and silver placed alternately over one another, the silver disc of one pair being separated from the zinc disc of the next by a piece of blotting paper moistened with brine. Such a pile, if composed of a sufficient number of pairs of discs, will produce electricity enough to give a shock, if the top and bottom discs, or wires connected with them, are touched with the moist fingers. This discovery placed at the disposal of the investigator a source of electricity by means of which experiments could be performed which had hitherto been impossible.

Shortly after the discovery of the voltaic pile, Nicholson and Carlisle* effected the decomposition of water, and Davy† isolated the alkali metals. As a result of these experiments, Davy was led to formulate his electrochemical theory. According to this theory, the atoms of different substances acquire opposite electrical charges by contact, and thus mutually attract each other. If the differences between the charges are small, the attraction will be insufficient to cause the atoms to leave their former positions; if it is great, a rearrangement of the atoms will occur, and a chemical compound will be formed. In terms of this theory, electrolysis consists in a neutralization of the charges upon the atoms.

The theory of Davy was soon superseded by that of Berzelius.‡ According to the latter theory, every atom is charged with both kinds of electricity, which exist upon the atoms in a polar arrangement, the electrical behavior of the atom being determined by the kind of elec-

* Nich. Jour., **4**, 179 (1800).

† Ibid., **4**, 275, 326 (1800); Gilb. Ann., **7**, 114 (1801).

‡ Gilb. Ann., **27**, 270 (1807).

tricity which is in excess. Chemical attraction is thus ascribed to the electrical attraction of oppositely charged atoms. Since each atom is endowed with both positive and negative electrification, one charge being in excess, it follows that the compound formed by the union of two or more atoms will be positively or negatively charged, according to whichever charge remains unneutralized after the atoms have combined. Two compounds, the one charged positively and the other negatively, may thus in turn combine, a more complex compound being formed. It was assumed that the atoms regained their charges when they were broken apart.

The ready substitution of chlorine for hydrogen in such compounds as acetic acid and chloroform constituted a serious objection to the theory. That negative charges could be substituted for positive charges without producing a more marked change in the properties of the material could not be satisfactorily explained. That positive hydrogen atoms combine with other positive hydrogen atoms to form hydrogen molecules, and that negative chlorine atoms combine with each other was a difficulty which was not cleared up until the advent of our present theories of atomic structure (Chapter XXIII).

Electrical Units. In 1827, Ohm enunciated his well-known law of electrical conductance, viz.: — *The strength of the electric current flowing in a conductor is directly proportional to the difference of potential between the ends of the conductor, and inversely proportional to its resistance.* If I represents the strength of the current, E the difference of potential, and R the resistance, then, with the proper choice of units, Ohm's law may be formulated as follows:

$$I = \frac{E}{R}. \qquad (1)$$

The unit of resistance is the *ohm*, that of difference of potential, or electromotive force, the *volt*, and that of current, the *ampere*. The ohm is defined as the resistance offered to an unvarying current by a column of mercury at 0° C., 14.4521 grams in mass, 106.300 centimeters in length, and of constant cross section. The ampere is defined as the current which will cause the deposition of 0.001118 gram of silver from a solution of silver nitrate in 1 second. The volt may be defined as the electromotive force necessary to drive a current of 1 ampere through a resistance of 1 ohm. The unit quantity of electricity is the *coulomb*. This amount of electricity passes when a current of 1 ampere flows for 1 second. One gram-equivalent of any ion carries 96,500 coulombs. This quantity of electricity is known as the *faraday* and is commonly represented by the letter F.

As has already been pointed out, any form of energy may be considered as the product of two factors, a capacity factor and an intensity factor. The capacity factor of electrical energy is the coulomb; the intensity factor is the volt, i.e.,

$$\text{electrical energy in joules} = \text{coulombs} \times \text{volts}.$$

It will be remembered that 1 *joule* is 10^7 *ergs*. Electrical energy may also be divided into a power factor, the *watt*, or *volt-ampere*, and a time factor, the second. One watt-second is 1 volt $\times$ 1 ampere $\times$ 1 second, or 1 joule. One kilowatt-hour is equal to 3,600,000 joules.

Direct experimental measurements have shown that 4.185 joules of electrical energy is equivalent to 1 calorie.*

In addition to these practical units we have the electrostatic units, e.s.u., and the electromagnetic units, e.m.u., which are used in some theoretical work but are not ordinarily used in practical electrochemistry. One electrostatic unit is the charge which will cause two point charges to repel each other with a force of 1 dyne when placed 1 centimeter apart in vacuo. The unit magnetic pole is of such strength that two such poles will repel each other with a force of 1 dyne when placed 1 centimeter apart in vacuo.

Electrical Conduction. There are two different types of electrical conduction: metallic conduction, as in the case of a copper wire; and electrolytic conductance, as in the case of a solution of salt in water. In the former case the electricity appears to be carried by a stream of electrons flowing toward the positive terminal. In the latter case the electricity is carried through the solution by ions. Positive ions move toward the negative electrode and negative ions move toward the positive electrode, and both share in carrying the current. In metallic conduction there is no change in the chemical properties of the conductor, but in electrolytic conductance, chemical reactions are produced at the electrodes and matter is transported to the electrodes.

Both types of electrical conductance involve the generation of more or less heat, depending on the electrical resistance of the system. As a general rule the metallic conductors become less conducting at high temperatures, whereas the electrolytic conductors become more conducting. In the former case, the electrons find it more difficult to pass through the crystal lattice when the units of the lattice are in thermal agitation; and in the latter case, the ions can move through the solution more readily because the viscosity is less and the solvation of the

* The international joule is referred to in these discussions: 1 int. joule = 1.00032 absolute joule.

ions is less. In some cases the number of ion carriers is increased also by an increase in temperature.

Electricity may be carried by electrons across an evacuated space as in an ordinary electron or radio tube. The electrons are emitted by a heated wire and drawn to a positively charged plate. Electricity may be carried also by means of gas ions, as in the case of an electrical discharge. The gas ions are charged positively and negatively, and they move in a manner somewhat analogous to the movement of electrolytic ions. There are several points of difference, however. Gas ions are produced by collisions in the electrical field, whereas the electrolytic ions are present before the electrodes are charged. The gas ions may have several different charges and there is little connection between the valence and the charge, whereas in the case of electrolytic ions the charge is closely connected with the valence.

Electrical resistance is directly proportional to the length of the conductor and inversely proportional to its cross section. The specific electrical resistance (the resistance of a cube 1 centimeter on an edge) of various materials is given for the sake of comparison in the following table:

ELECTRICAL RESISTANCE OF TYPICAL CONDUCTORS

Material	Temperature	Specific Resistance
Silver	0°	1.468×10^{-6} ohm
Copper	0°	1.561×10^{-6}
Aluminum	0°	2.563×10^{-6}
Iron	0°	9.065×10^{-6}
Lead	0°	$20\ 380\times10^{-6}$
Mercury	0°	95.80×10^{-6}
Fused $NaNO_3$	500°	0.568
Fused $ZnCl_2$	500°	11.93
1 *M* KCl	25°	8.942
0.001 *M* KCl	25°	7083.
1 *M* Acetic acid	18°	757.5
0.001 *M* Acetic acid	18°	24,400.
Water	18°	25×10^{6}

Faraday's Law. When two platinum electrodes, one connected to the positive and the other to the negative terminal of a battery, are immersed in a solution of sodium chloride, hydrogen is evolved at the negative electrode and oxygen at the positive electrode. If the salt solution is previously colored with a few drops of a solution of litmus, it will be observed that the portion of the solution in the neighborhood

of the positive electrode turns red, indicating the formation of an acid, while that in the neighborhood of the negative electrode turns blue, showing the formation of a base. The same changes take place whether the electrodes are placed near together or far apart, and furthermore, the evolution of gas and the change in color at the electrodes commences as soon as the circuit is closed. The study of these phenomena led Faraday in 1834 to the conclusion that, when an electric current traverses a solution, there occurs an actual transfer of matter, one portion traveling with the current, and the other portion moving in the opposite direction. Faraday termed these carriers of the current, *ions*. He called the electrode connected to the positive terminal of the battery, the *anode*, and the electrode connected to the negative terminal, the *cathode*. The ions which move toward the anode he called *anions*; those which migrate toward the cathode he called *cations*. The whole process he termed *electrolysis*. As a result of his experiments he enunciated the following laws:

(1) For the same electrolyte, the amount of electrolysis is proportional to the quantity of electricity which passes.

(2) The amounts of substances liberated at the electrodes, when the same quantity of electricity passes through solutions of different electrolytes, are proportional to their chemical equivalents.

On the basis of very accurate experimental measurements, Faraday's law may now be stated as follows:

In electrolysis, 96,500 *coulombs of electricity produce a chemical change* of 1 *gram-equivalent.** For example, 96,500 coulombs (or ampere-seconds) will liberate 1.008 g. of hydrogen, and it will deposit from solution 107.88 g. of silver, 63.57/2 g. of copper from cupric salts, and 197.2/3 g. of gold from auric solutions. The name Faraday and the symbol F are given to this important quantity of electricity.

This law is one of the most exact laws in physical chemistry; it has been found to hold at low and high temperatures, in dilute and concentrated solutions, at various pressures and in different solvents.

Faraday's law can be clearly understood with the help of the hypothesis that atoms are composed of positive nuclei surrounded by negative electrons. When an electron is removed from an atom, the remaining ion is positively charged. When an extra electron becomes attached to an atom, a negative ion is produced. If two electrons are involved, the ions are bivalent.

The reactions may be illustrated by the following equations, in which an electron is represented by e,

* One gram-equivalent = atomic weight in grams ÷ valence.

$Ag = e + Ag^+ = 1$ electron + 1 univalent positive silver ion. (2)

$Cu = 2e + Cu^{++} = 2$ electrons + 1 divalent positive copper ion. (3)

$Cl + e = Cl^- = 1$ univalent negative chloride ion. (4)

Now in electrolysis, electrons are supplied to the cathode and removed from the anode. This change is produced either by a chemical reaction in an external battery, or by the mechanical operation of a magnet in a dynamo. When cupric chloride is dissolved in water, each of the two chlorine atoms holds an extra electron obtained originally from the copper atom. Every time two electrons are supplied to the cathode they become attached to one of the cupric ions which happens to be in contact with the cathode and equation (3) is reversed; i.e., an atom of copper is formed from the cupric ion and deposits on the electrode.

For every electron supplied to the cathode, one electron is withdrawn from the anode. These electrons are taken from the chloride ions in contact with the anode, and in this way equation (4) is reversed. Two chlorine atoms produced in this way from two chloride ions combine to give a chlorine molecule, which is liberated at the anode, or dissolved in the solution.

Electrolysis involves, then, a transfer of electrons between the electrodes and the surrounding ions, and Faraday's law is simply the result of counting off one electron for each univalent atom, or two electrons for each divalent ion, etc. Each gram-atom contains 6.06×10^{23} atoms, and accordingly 6.06×10^{23} electrons are involved in its electrolysis. The charge on the electron is 1.59×10^{-19} coulombs (Chapter XXI), and so the coulombs required to electrolyze a gram-atom of a univalent ion are

$$6.06 \times 10^{23} \times 1.59 \times 10^{-19} = 96{,}500 \text{ coulombs.}$$

This number is in agreement with the value already given. As a matter of fact, the experimental determination of the value of the faraday and the charge on the electron provide our best means for determining the value for the Avogadro number, 6.06×10^{23}.

If a divalent ion, like copper, is deposited, two electrons are required for each ion, and one faraday deposits only one-half of a gram-atom, i.e., one equivalent.

Since Faraday's law involves only a counting process, it is evident why the law is so exact. Its accuracy is limited only by the accuracy of measuring the chemical change and the quantity of electricity.

Faraday's law applies only to the primary change — the one involving the electron transfer. The final materials produced by the

electrolysis depend on the chemical reactions which follow the electrolysis and some chemical experience is necessary in predicting just what will happen. For example, if chlorine is liberated in an alkaline solution, hypochlorite or chlorate may be formed. If chlorine is liberated on a silver anode, silver chloride will be formed.

If a copper anode is used in the electrolysis of a solution of cupric chloride, the copper will simply go into solution and take the place of that which is removed at the cathode. If a platinum anode is used, the platinum cannot go into solution and oxygen is liberated from the water. When several different ions are competing for the transfer of an electron, several possibilities occur, depending on the concentration and on the energies involved. This problem will be discussed in a later chapter.

Coulometers. The quantity of electricity passing through an electric circuit is measured by means of an electrolytic cell, which is so arranged as to allow the amount of chemical change occurring at an electrode surface to be accurately determined. Such a cell is known as a *coulometer*. There are three general types of coulometers in use, namely, (1) *weight coulometers*, in which the quantity of electricity is measured by the gain in weight of the cathode due to the deposition of metal from the electrolyte; (2) *volume coulometers*, in which the volume of hydrogen or oxygen gas liberated by the passage of the current is measured; and (3) *titration coulometers*, in which the change in concentration of the electrolyte at one of the electrodes is determined by titration with a standard solution.

Of these three types, the most accurate is the silver coulometer in which silver is deposited from a solution of silver nitrate upon a weighed platinum dish as a cathode.* For industrial purposes the copper coulometer is usually employed. This is also a weight coulometer, and consists of two sheets of pure copper as an anode between which is placed a single weighed sheet of thin copper as a cathode, while a solution of copper sulphate serves as the electrolyte.

The iodine coulometer is an example of the third type. The iodine liberated at the platinum anode from a solution of potassium iodide is titrated with sodium thiosulphate.

The Migration of Ions. For every electron supplied at the cathode, one electron is removed at the anode, and so it is obvious that the same amount of electrochemical action must occur at each electrode. The passage of the current through the solution, however, does not depend on the action at the electrodes. The current is carried by negative ions, with extra electrons, moving toward the anode, and by positive

* Bull. Bur. Standards, **1**, 3 (1904).

ions, which have lost electrons, moving toward the cathode. Both are instrumental in carrying the current, and it is interesting to learn which carries the larger fraction.

This matter is determined by the relative velocities with which the two ions move. It is obvious that as long as the solution is uncharged the number of positive and negative ions must be equal in the solution as a whole, but the concentration of both positive and negative ions may vary between the two electrodes. The ions which move faster carry the larger quantity of electricity across the solution in a given time; i.e., they carry the larger fraction of the current. If u is the relative velocity of the cation and v is the relative velocity of the anion, then the total quantity of electricity transferred will be proportional to $u + v$. Of this total, the fraction, n_a, carried by the anion, will be $v/u + v$ and the fraction, n_c, carried by the cation, will be $u/u + v$. Furthermore, $n_c + n_a = 1$, and $n_c = 1 - n_a$. These ratios, n and $1 - n$, are called the Hittorf transference numbers, or transport numbers, because the subject was first effectively investigated by Hittorf in 1853.

In dilute hydrochloric acid at room temperature $n_a = 0.17$ and $n_c = 0.83$. In other words, the hydrogen ion carries about five times as much of the current as the chloride ion, and in order to do this it must move five times as fast.

During electrolysis the concentration around the electrode is changed both by the chemical changes taking place at the electrodes and by the migration of the two ions at different velocities. The way in which these changes are effected is illustrated diagrammatically in Fig. 117. The system undergoing electrolysis is divided into three compartments with imaginary partitions. The concentration is uniform throughout the vessel before the electrolysis, and it is assumed that there are six positive ions and six negative ions in each compartment.

In the first case, I*A* and I*B*, it is assumed that the two ions move with equal velocities ($n_a = n_c = 0.5$), and that the current is passed long enough to deposit six ions — i.e., six electrons are removed from the anode and supplied to the cathode. The current is carried by both positive and negative ions and in this case both move with equal velocities and each carries half of the current. Accordingly, three charges are carried across by the cations and three charges are carried across in the opposite direction by the anions. The movement of the ions is indicated by dotted arrows in I*A* and the net result is shown in I*B*. Six cations have been deposited at the cathode, three have moved into the cathode compartment from the middle compart-

ment, and three have moved into the middle compartment from the anode compartment. Similar changes occur with the anions. The net result of migration and electrolysis is to decrease the concentration in the neighborhood of the electrodes from six to three and to leave the concentration unchanged in the middle compartment.

When the transference numbers of the two ions are not equal, the change in concentration is different at the two electrodes, as shown in

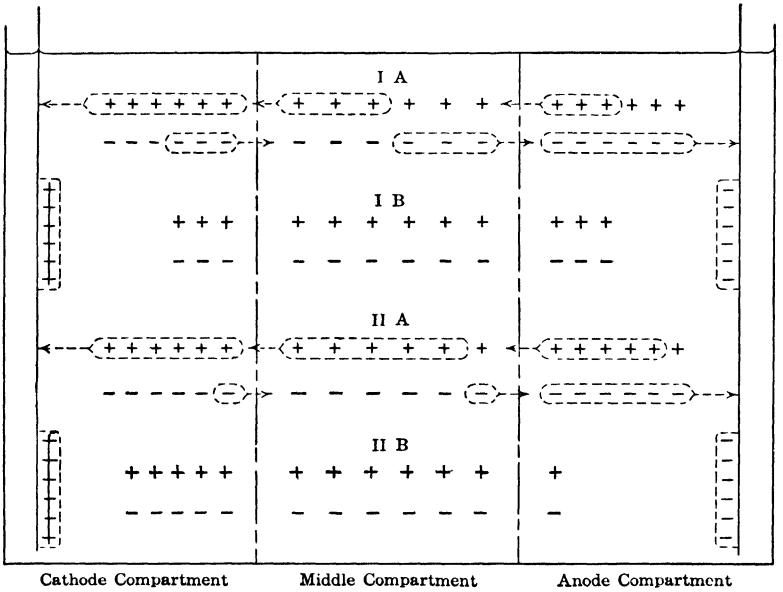


FIG. 117

II*A* and II*B*. It may be imagined that the electrolyte is hydrochloric acid in water and that the positive hydrogen ions move five times as fast as the negative chloride ions. Each of the three compartments holds six positive and six negative ions. Six ions are discharged at each electrode, as before, but in this case five-sixths of the current is carried by the hydrogen ions and only one-sixth by the chloride ions. The changes are indicated by dotted lines and arrows in II*A* and the net result is shown in II*B*. Six hydrogen ions are discharged at the cathode but five move in from the middle compartment, leaving the concentration five-sixths as large as before electrolysis. Six chloride ions are discharged but only one migrates into the anode compartment, and the concentration around the anode is only one-sixth as large as before.

Experimental Determination of Transference Numbers. Transference numbers are readily determined by measuring the change in concentration at the electrodes and correcting for the change produced by the chemical reaction at the electrodes. In this way the changes caused by the migration of the ions are obtained and these in turn are related to the velocities, as expressed by the following proportion,

$$\frac{\text{Change in concentration at anode due to migration}}{\text{Change in concentration at cathode due to migration}} = \frac{\text{speed of cation}}{\text{speed of anion}} = \frac{u}{v}.$$

The relation between velocities and transference numbers has been given before.

In carrying out a determination, the cell is filled and connected to a source of current through a variable resistance, a silver coulometer and a milliammeter as shown in Fig. 118. The current is allowed to pass until a sufficient change in concentration has taken place, as determined with the help of the milliammeter. The change in concentration is obtained by comparing the final concentrations with the original concentrations or with the solution in the middle compartment.

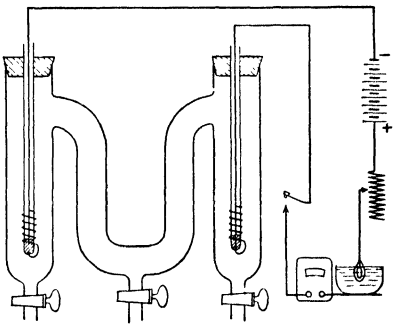


FIG. 118

The following example will serve to make the method of calculation clear: — In an experiment to determine the transference numbers of the ions of silver nitrate, a solution containing 0.00739 gram of that salt per gram of water was prepared. The solution was introduced into the migration apparatus and, after inserting silver electrodes, a small current was passed through the apparatus for two hours. A silver coulometer was included in the circuit, and 0.0780 gram of silver was deposited by the current. This mass of silver is equivalent to 0.000723 gram-equivalent. After the circuit was broken, the anode solution was rinsed out and its concentration determined analytically. It was found to contain 0.2361 gram or 0.001391 gram-equivalent of silver nitrate to 23.14 grams of water. This amount of solution contained originally $23.14 \times 0.00739 = 0.1710$ gram (0.001008 gram-equivalent) of silver nitrate. If none of the silver ions moved away from the anode, the final quantity of silver in the anode compartment

would be 0.001008 + 0.000723 = 0.001731 gram-equivalent, since 0.000723 gram-equivalent was dissolved from the anode. Actually the amount found at the end of the experiment was 0.001391 gram-equivalent; hence 0.001731 − 0.001391 = 0.000340 gram-equivalent must have migrated away. At the same time enough nitrate ions, namely 0.001391 − 0.001008 = 0.000383 gram-equivalent, must have entered the anode compartment to make the solution electrically neutral at the end of the experiment. But 0.000723 gram-equivalent of silver measures the total quantity of electricity transported, therefore the transference numbers of the two ions will be as follows:

$$\text{Transference number of } Ag^+ = n_c = \frac{0.000340}{0.000723} = 0.470,$$

$$\text{Transference number of } NO_3^- = n_a = \frac{0.000383}{0.000723} = 0.530.$$

These numbers can be checked by a similar calculation based on the change in concentration in the cathode compartment.

The accompanying table gives the transference numbers of the cations of several typical electrolytes, at different concentrations and different temperatures. The transference numbers of the corresponding anions can be found by subtracting the transference numbers of the cations from unity.

It is apparent from the table that the transference numbers are not entirely independent of the concentration, and also that they vary slightly with the temperature. In fact, with rising temperature, the transference numbers of all ions tend to become equal, the limiting value being 0.5.

Transference Numbers and Ionic Hydration. In the method just outlined for the determination of transference numbers, it was assumed that the solvent remains stationary during the passage of the current, and that the change in concentration which occurs in the vicinity of the electrode is due to the difference in the relative speeds with which the ions move through the solution.

That this assumption is not correct has been proved by Washburn and Millard,* who have demonstrated experimentally that the ions are hydrated and carry a portion of the solvent with them from one electrode to the other. Although the amount of solvent thus transferred, in dilute solutions, is exceedingly small, it becomes sufficiently large, in concentrated solutions, to affect the values of the transference numbers. If an inert substance, such as sucrose, is added to the solu-

* J. Am. Chem. Soc., **37**, 694 (1915).

TRANSFERENCE NUMBERS OF CATIONS*

Electrolyte	Temp.	Concentration					
		0.005	0.01	0.02	0.05	0.10	0.20
NaCl	0°	0.387	0.387	0.387	0.386	0.385	....
	18	0 397	0.397	0 396	0.393	0.390	....
	30	0.404	0.404	0.404	0.404	0.403	....
KCl	0	0.493	0.493	0.493	0.493	0.492	0.491
	18	0.496	0.496	0.496	0.496	0.495	0.494
	30	0.498	0 498	0.498	0.498	0.497	0.496
LiCl	18	.....	0 332	0.328	0.320	0.313	0.304
NH_4Cl	18	.....	0.492	0.492	0.492	.....	.....
$AgNO_3$	18	.....	0.471	0 471	0.471	0.471	.....
	30	0.481	0.481	0.481	0.481	0.481	0.481
HCl	0	0.847	0.846	0.844	0.839	0.834	.....
	18	0.832	0 833	0.833	0.834	0.835	0.837
HNO_3	20	0.839	0 840	0.841	0.844	.....	.....
$BaCl_2$	0	0.439	0.437	0.432	.....	.....	.....
	25	.....	.....	.....	0.438	0.427	0.415
$CaCl_2$	20	0.440	0.432	0.424	0.413	0.404	0 395
H_2SO_4	20	.....	.. ..	0.822	0.822	0.822	0.820
$MgSO_4$	18	0.388	0.385	0.381	0.373	.....	.....
$CuSO_4$	18	.. .	.....	0.375	0.375	0.373	0.361

* Noyes and Falk, J. Am. Chem. Soc., **33,** 1454 (1911).

tion in a transference experiment, it will remain stationary during the passage of the current, and may be used as a reference substance to determine the amount of solvent which has been transported by the ions. In this manner, Washburn and Millard determined the so-called "true" transference numbers. In dilute solutions, the difference between the Hittorf transference number n_c and the true transference number n_c' is so small as to be negligible. If n_w denotes the number of mols of water transferred from the anode to the cathode per faraday of electricity, and N_s/N_w is the ratio of the number of mols of the solute to the number of mols of water in the original solution, the relation between the Hittorf transference number of the anion, n_a, and the true transference number of the anion, n_a', will be given by the equation,

$$n_a' = n_a - n_w \frac{N_s}{N_w} \tag{5}$$

TRUE TRANSFERENCE NUMBERS AT 25°

Electrolyte Concentration 1.3 Molar	n_w/n_c'	n_w	n_c'	n_∞	n_c
HCl	0.28	0.24	0.844	0.833	0.820
CsCl	0 67	0.33	0 491	0.491	0.485
KCl	0.3	0.60	0.495	0.495	0.482
NaCl	2.0	0.76	0.383	0.396	0.366
LiCl	4.7	1 5	0 304	0.330	0.278

Specific, Molar and Equivalent Conductance. The *specific resistance* of an electrolyte may be defined as the resistance in ohms of a column of solution one centimeter long and one square centimeter in cross section. *Specific conductance* is the reciprocal of specific resistance. Since the conductance of a solution is almost wholly dependent upon the amount of solute present, it is more convenient to express conductance in terms of the molar, or equivalent concentration. The *molar conductance*, μ, is the conductance, in reciprocal ohms,* of a solution containing 1 mol of solute when placed between sufficiently large electrodes which are exactly 1 centimeter apart. The *equivalent conductance*, Λ, is the conductance, in reciprocal ohms, of a solution containing 1 gram-equivalent of solute when placed between electrodes which are 1 centimeter apart. If L denotes the specific conductance of a solution, and V_m the volume in cubic centimeters which contains 1 mol of solute, then

$$\mu = LV_m, \tag{6}$$

and in like manner,

$$\Lambda = LV_e, \tag{7}$$

where V_e is the volume of solution in cubic centimeters which contains 1 gram-equivalent of solute. If C denotes the concentration of a solution of an electrolyte in gram-equivalents per liter, equation (7) becomes,

$$\Lambda = \frac{1000\,L}{C}. \tag{8}$$

The following table gives the specific and equivalent conductance of solutions of sodium chloride at 18° C.:

* Reciprocal ohms are sometimes called mhos.

CONDUCTANCE OF SOLUTIONS OF SODIUM CHLORIDE

Concentration	Dilution	Sp. Cond.	Molar Cond.
1	1,000	0.0742	74.2
0.1	10,000	0.00918	91.8
0.01	100,000	0.001017	101.7
0.001	1,000,000	0.0001063	106.3
0.0001	10,000,000	0.00001079	107.9

It will be observed that the specific conductance decreases as the concentration decreases, but that the molar conductance increases with the dilution at first and then approaches a limiting value.

The reason for these facts may be illustrated by imagining a rectangular cell of indefinite height having a cross-sectional area of 1 square centimeter. Two opposite walls function as electrodes and 1000 cubic centimeters of a solution containing 1 mol of a completely ionized solute is introduced into the cell. The specific conductance is the conductance of a section 1 centimeter high, but the molar conductance of a molar solution is the conductance of the whole cell, 1000 centimeters high. When 1 liter of a dilute solution of salt is diluted to 2000 cubic centimeters, there are half as many ions in each centimeter cube as before and the specific conductance is reduced to one-half of its original value. The solution stands at twice the original height in the cell, however; the electrode surface in contact with the solution is doubled; and the total conductance due to 1 mol of solute remains unchanged if the solution is already very dilute.

The molar conductance is smaller in concentrated solutions on account of an interionic attraction between the ions. In the case of weak electrolytes it is *much* smaller because the solute molecules are only partially ionized and the extent of the ionization increases as the dilution is increased.

Determination of Electrical Conductance. The determination of the electrical conductance of a solution resolves itself into the determination of its resistance by a simple modification of the familiar Wheatstone bridge method. The arrangement of the apparatus devised originally by Kohlrausch in 1880 is shown in Fig. 119; C is the cell containing the solution whose resistance is to be measured and A is a resistance box. Alternating current of about a thousand cycles, which gives a high mosquito-like tone in the telephones T, is generated by a

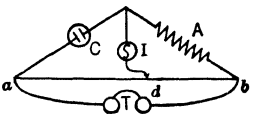


FIG. 119

battery and the microphone hummer shown at I. This hummer contains a magnet in the form of an electrically operated tuning-fork which induces currents in an adjacent coil of wire. In the earlier work a small induction coil was used at I. Alternating current is necessary to prevent the polarization of the electrodes which occurs when direct current is used.

In making a measurement, the resistance A is adjusted and the sliding contact d is moved along the wire ab until the sound in the telephone reaches a minimum when the position of the point of contact is read on the scale. Under these conditions a and b must be at the same potential and, according to the principle of the Wheatstone bridge, the resistances are given by the following proportion:

$$\frac{C}{A} = \frac{ad}{bd}. \tag{9}$$

Since the resistance A and the lengths bd and ad are known, the resistance C can be calculated.

Many improvements have been introduced leading to greater convenience or greater accuracy.* The wire is coiled on a cylindrical drum and the point of contact is moved by rotating the drum. In some bridges the wire is arranged in a series of contacts, each contact representing multiplication by a factor of ten, and the bridge ratio ad/bd merely locates the decimal point. The resistance A is changed by turning a number of dials. In accurate measurements a variable capacity is placed across the resistance A and adjusted to offset the capacity in the cell C and give a minimum of sound at the point of balance. The most accurate results are obtained by using amplifiers and an oscillating circuit produced with a system of electron tubes, capacities and large inductances.

One of the simplest cells consists of two circular platinum plates in a cylindrical cell. Connection is made through stout platinum wires sealed through the ends of glass tubes, a drop of mercury in each making contact with the copper wires of the circuit. The tubes are set firmly into a vulcanite cover so that the electrodes may be removed, rinsed and dried without altering their relative positions.

Washburn† pointed out that in order to obtain the best results the cross section of the cell should be adjusted to the circuit. Three types of conductance cells are shown in Fig. 120: A is adapted for specific conductances as low as 1×10^{-6} reciprocal ohm, B for conductances

* The matter of accuracy is discussed fully by Jones and Josephs, J. Am. Chem. Soc., **50**, 1049 (1928).

† J. Am. Chem. Soc., **38**, 2431 (1916).

ranging from 10^{-6} to 10^{-3}, and C for conductances ranging from 10^{-4} to 10^{-1}.

The electrodes are usually coated, electrolytically, with platinum black to adsorb gases and eliminate any possible polarization due to imperfect alternating current. If the current is of the pure sine wave type as generated with electron tubes, the platinizing may be unnecessary.

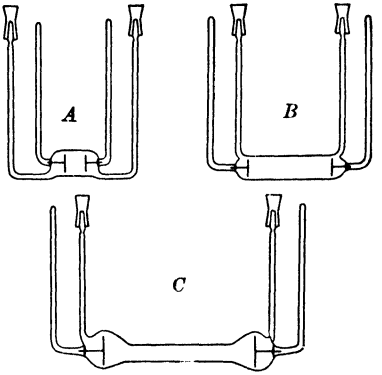


FIG. 120

It is not necessary to know the area of the electrodes or the distance between them since it is possible to determine a factor, called the *cell constant*, by means of which the results obtained with the cell can be transformed into reciprocal ohms. The resistance of the cell is measured when it contains a solution of known specific conductance, and for this purpose a 0.02 molar solution of potassium chloride is generally used. It has the following specific conductances:

$$L_{18^\circ} = 0.002394, \quad \text{and} \quad L_{25^\circ} = 0.002761 \text{ reciprocal ohms.}$$

The specific conductance L of a solution is proportional to the measured conductance, and if R is the resistance of the cell, when filled with 0.02 molar potassium chloride, $1/R$ is the conductance and

$$L = K\frac{1}{R}, \tag{10}$$

or

$$K = L\,R, \tag{11}$$

where K is the proportionality constant or cell constant converting measured conductance into specific conductance.

With 0.02 molar potassium chloride at 25°

$$K = 0.002761\,R. \tag{12}$$

The specific conductance of any solution is then obtained directly by dividing the cell constant by the observed resistance.

Relative Conductances of Different Substances. The study of the electrical conductance of various solutes in aqueous solution reveals the fact that electrolytes differ greatly in their conducting power. They may be roughly divided into two classes: those with high

conducting power, such as strong acids, strong bases, and salts; and those with low conducting power, such as ammonia, and most of the organic acids and bases. The following table gives the equivalent conductances of several typical electrolytes, from normal down to so-called "zero" concentration. In every case it will be observed that the equivalent conductance increases with the dilution of the solution until a limiting value, Λ_0, is reached. It is important to bear in mind that, although Λ_0 is frequently referred to as the conductance at infinite dilution, it is not identical with the conductance of the pure solvent.

In the case of so-called "strong electrolytes," the value of the limiting conductance, Λ_0, is obtained by extrapolating the values of the conductance at finite concentrations. Although the accuracy of extrapolated data is always more or less uncertain, the error in the extrapolated values of Λ_0, for strong electrolytes, is probably within 1 per cent, in the majority of cases. To minimize the error in extrapolation, Noyes and Falk* plotted the reciprocal of the equivalent conductance, $1/\Lambda$, against $(C\Lambda)^n$ and then, by trial, determined the value of n which would give a straight line. (C is the concentration in equivalents per liter.) On extending this line until it cuts the axis at a point corresponding to $(C\Lambda)^n = 0$, the limiting value of $1/\Lambda$ was found, and from this the value of the limiting conductance, Λ_0, could easily be calculated. The value of n was found to be approximately 0.5.

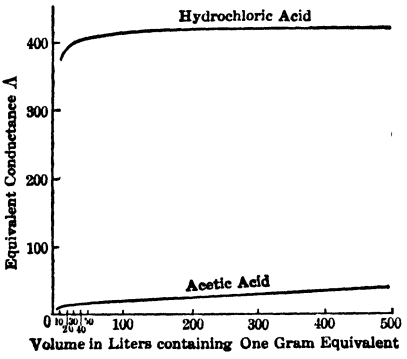


FIG. 121

The limiting conductance of weak electrolytes cannot be determined by the method just outlined, owing to the fact that, at concentrations below 0.0001 molar, it is very difficult to make satisfactory measurements of conductance, and consequently the method of extrapolation cannot be employed. In order to determine the value of Λ_0, for weak electrolytes, it is necessary to know the values of the conductance of the individual ions, as determined by the law of Kohlrausch.

Some of these data are shown graphically in Figs. 121 and 122, where it will be noted that the equivalent conductance of the strong electrolytes reaches a limiting value at the higher dilutions. The weak electrolytes, such as acetic acid, however, do not reach such a limiting

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

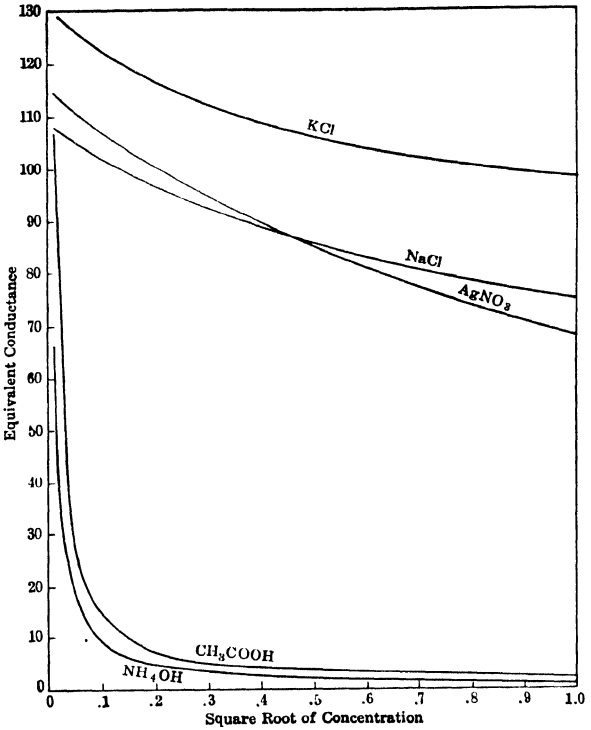


FIG. 122

EQUIVALENT CONDUCTANCES

Temp. 25°

Normal conc.	NaCl	KCl	HCl	$AgNO_3$	HNO_3	$\frac{1}{2}Na_2SO_4$	$\frac{1}{2}H_2SO_4$	$HC_2H_3O_2$	NH_4OH
0.0000	.....	148.8	424.7	132.9	420.4	129.3	428.7	390.8	271
0.0001	.....	.....	424.6	.....	.....	.....	.....	134.7	93
0.0005	125.0	.....	.....	.....	.....	.....	413.1	67.7	47
0.0010	124.1	147.4	.....	130.1	.....	.....	399.5	49.2	34
0.0020	123.0	146.3	.....	128.7	.....	122.1	390.3	35.5	25
0.0050	120.8	143.8	415.6	126.6	411.2	117.3	364.9	22.9	16
0.0100	118.6	141.2	412.0	124.1	407.3	112.4	336.4	16.3	11.3
0.0200	115.8	138.0	407.3	120.9	402.4	106.8	308.0	11.6	8.0
0.0500	111.0	133.1	399.0	115.0	394.0	97.8	272.6	7.4	5.1
0.1000	106.6	128.6	391.3	108.7	386.0	90.0	250.8	.....	3.6
0.2000	101.5	123.9	381.3	101.8	376.1	81.5	234.3	.....	.....
0.5000	93.3	117.2	360.6	.....	356.5	.....	222.5	.....	.....
1.0000	.....	111.9	331.9		329.8				

value within regions which can be studied experimentally. Below concentrations of 0.0001 molar the conductance of the solvent itself becomes relatively large and traces of carbon dioxide or ammonia from the air, or alkali from the glass introduce large errors.

The Law of Kohlrausch. The electrical conductance of solutions was systematically investigated by Kohlrausch who showed that the limiting value of the equivalent conductance, which may be represented by Λ_0, is different for different electrolytes, and may be considered as the sum of two independent factors, one of which refers to the cation and the other to the anion. This experimental result is commonly known as the law of Kohlrausch.

The limiting value of the equivalent conductance is reached when the molecules are completely broken down into ions, and, under these conditions, the whole of the electrolyte participates in conducting the current. The accompanying table, giving the equivalent conductances at infinite dilution of several binary electrolytes, illustrates the truth of the law of Kohlrausch.

EQUIVALENT CONDUCTANCES AT INFINITE DILUTION
Temp. 18°

	K	Na	Li	NH_4	H	Ag
Cl	129	108	98	129	380	.....
NO_3	126	105	.....	.....	377	115
OH	238	217	.....	.....	.....	.....
ClO_3	119	.....	.....	.....	.....	109
$C_2H_3O_2$	99	78	.....	.....	.....	89

The differences between two corresponding sets of numbers in the same vertical column, or between any two corresponding sets of numbers in the same horizontal row, will be found to be nearly equal. This could occur only when the limiting conductance represents the sum of two entirely independent quantities.

Each ion invariably carries the same charge of electricity, and moves with its own velocity, quite independently of the nature of its companion ion. Therefore, at infinite dilution, we have

$$\Lambda_0 = l_c + l_a, \tag{13}$$

in which l_c and l_a are the equivalent conductances of the ions of the electrolyte at infinite dilution. From this it follows that

$$n_a = \frac{l_a}{l_c + l_a} = \frac{l_a}{\Lambda_0}, \tag{14}$$

and $$n_c = \frac{l_c}{l_c + l_a} = \frac{l_c}{\Lambda_0}; \quad (15)$$

or $$l_a = n_a \Lambda_0, \quad (16)$$

and $$l_c = n_c \Lambda_0. \quad (17)$$

Thus, the equivalent conductance of silver nitrate at infinite dilution, at 18°, is 115.6, while $n_a = 0.534$ and $n_c = 0.466$; therefore,

$$l_a = 0.534 \times 115.6 = 61.7,$$

and $$l_c = 0.466 \times 115.6 = 53.9;$$

or, 1 gram-equivalent of NO_3 ions possesses a conductance of 61.7, when placed between electrodes 1 centimeter apart, and large enough to contain between them the entire volume of solution in which the NO_3^- ions exist. Under the same conditions, 1 gram-equivalent of Ag^+ ions has a conductance equal to 53.9.

The values of the ionic conductances, at infinite dilution, remain constant in all solutions in the same solvent at the same temperature, so that it is possible to calculate the equivalent conductance for any substance at infinite dilution.

In the subjoined table are given the ionic conductances of various ions at 18° and infinite dilution, together with their temperature coefficients.

IONIC CONDUCTANCES AT INFINITE DILUTION
Temp. 18°

Ion	l	$\frac{1}{l}\left(\frac{dl}{dt}\right)_{18}$	Ion	l	$\frac{1}{l}\left(\frac{dl}{dt}\right)_{18}$
Li^+	33.0	0.0265	ClO_3^-	54.9	0.0215
Na^+	43.2	0.0244	IO_3^-	33.8	0.0234
K^+	64.3	0.0217	NO_3^-	61.7	0.0205
Rb^+	67.6	0.0214	H^+	315.2	0 0157
Cs^+	67.5	0.0212	OH^-	173.8	0.0180
NH_4^+	64.5	0.0222	$\frac{1}{2}Zn^{++}$	45.6	0.0251
Tl^+	65.5	0.0215	$\frac{1}{2}Mg^{++}$	45.0	0.0256
Ag^+	53.9	0.0229	$\frac{1}{2}Ba^{++}$	55.0	0.0238
Cl^-	65.3	0.0216	$\frac{1}{2}Pb^{++}$	61.0	0.0243
Br^-	67.4	0.0215	$\frac{1}{2}SO_4^{--}$	68.0	0.0227
I^-	66.3	0.0213	$\frac{1}{2}CO_3^{--}$	70.0	0.0270

In the case of weak electrolytes, the value of Λ_0 cannot be determined directly from conductance measurements, since the solution becomes so dilute before the limiting value of the conductance is

reached that accurate measurements of the specific conductance are impossible. However, the law of Kohlrausch enables us to overcome this difficulty. Thus, the value of Λ_0 for acetic acid must be equal to the sum of the conductances of the H^+ and CH_3COO^- ions. The conductance of the H^+ ion at 18° is 315, according to the preceding table, while the value of the conductance of sodium acetate at infinite dilution is 78.1 at 18°. Since the ionic conductance of the Na^+ ion is 43.2 at 18°, it follows that the conductance of the CH_3COO^- ion must be 78.1 − 43.2 = 34.9. Therefore, for acetic acid, we have

$$\Lambda_0 = l_c + l_a = 315 + 34.9 = 349.9 \text{ at } 18°.$$

Bredig* showed that the ionic conductance of elementary ions is a periodic function of the atomic weight. Since the atomic number†

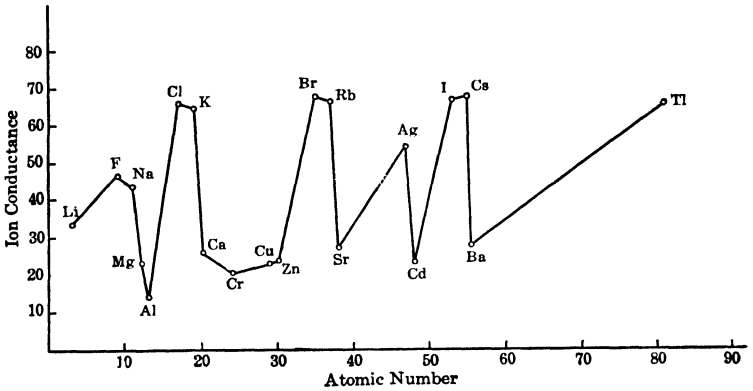


FIG. 123

rather than the atomic weight is now known to be the fundamental property of the atom, the ionic conductances of the atoms studied by Bredig are plotted against their atomic numbers instead of their atomic weights in Fig. 123. A glance at the curve shows the periodic nature of the relation.

Conductance and Ionization. As stated in an earlier chapter (p. 197) Arrhenius, in 1887, showed that only those solutions conduct the electric current which exert abnormally large osmotic pressures. It had already been pointed out by Kohlrausch that the equivalent conductance of a solution increases initially with the dilution and approaches a constant value. Arrhenius explained this behavior by assuming that the molecules of the solute undergo dissociation into ions. The degree of dissociation increases with the dilution until finally, when the

* Z. physik. Chem., **13**, 242 (1894).

† The term "atomic number" is defined in Chapter XXI.

equivalent conductance has reached its maximum value, the molecules of solute become completely broken down into ions.

It has been shown in equation (13) that the equivalent conductance at infinite dilution Λ_0 is the sum of the ionic conductances, l_c and l_a,

$$\Lambda_0 = l_c + l_a. \tag{18}$$

Neglecting the change in velocity of the ions with concentration, and assuming that the only influence of dilution on the equivalent conductance is the production of more ions, Arrhenius stated that at any dilution

$$\Lambda = \alpha\,(l_c + l_a), \tag{19}$$

where α is the degree of dissociation. Dividing equation (19) by equation (13)

$$\alpha = \frac{\Lambda}{\Lambda_0}. \tag{20}$$

This equation of Arrhenius has been widely used for calculating the degree of dissociation of an electrolyte at any concentration from the ratio of the equivalent conductance at that concentration to the equivalent conductance at infinite dilution. It is still adequate for weak electrolytes in dilute solutions, but it is now realized that equation (20) has no theoretical justification when applied to solutes which are largely ionized. It has been shown (p. 199) that in the case of these strong electrolytes the interionic attraction is a large factor in the osmotic properties, and it is also a large factor in slowing down the velocity of the ions when placed between electrodes. Each negative ion attracts a sphere of positive ions which pile up behind it as it moves toward the positive electrode and retard its motion, and each positive ion is dragged back in the same way with negative ions. As the dilution is increased, the ions become farther and farther apart, the interionic attraction becomes less and the velocity increases.

At great dilutions the interionic attraction is negligible and the ions have their maximum velocities, uninfluenced by further dilution.

The theory of Arrhenius was so satisfactory for weak electrolytes that it exerted a considerable influence in the study of strong electrolytes, even though there were obvious difficulties which will be described later. It seems strange that the effect of dilution on the conductance was attributed, for such a long time, *only* to the number of ions while the obvious effect on the velocities was entirely neglected. It is evident from the table of transport numbers on p. 371 that the velocities are affected by concentration, and the velocities as well as the number of ions determine the electrical conductance. As far back

as 1900 Jahn* questioned the validity of the constancy of ionic mobilities. In 1904, A. A. Noyes,† who has been a leader in the study of the electrical conductivity of solutions, stated that "this [research] gives support to the idea that the decrease of conductivity and of the calculated dissociation is due to a physical cause (probably in some way to the electrical charges on the ions) and not to specific chemical affinity." Kahlenberg has objected for many years to the Arrhenius theory.

Recently the pendulum has swung too far in the other direction and some authors have inferred that all strong electrolytes are completely dissociated at all concentrations and that the only effect of increasing concentration is to decrease the velocity of the ions through the interionic attraction. There is good evidence, however, that many strong electrolytes such as magnesium sulphate and hydrochloric acid are only partially dissociated in moderately concentrated solution. Cadmium chloride and particularly mercuric chloride are only partially dissociated in moderately concentrated solution. The arrangement of atoms, or ions, of the crystal lattice in the solid state is an important factor in determining whether or not a solute will dissociate when it dissolves in water.

In dilute solutions of strong electrolytes where the interionic attraction is the predominating factor, the conductance ratio Λ/Λ_0 is largely affected by the valence type. When two or more charges reside on a single ion, the interionic attraction is greater and the deviation from ideal behavior (infinite dilution) is partly determined by the ionic strength μ (p. 200). The following table illustrates this relationship.

CONDUCTANCE RATIO OF TYPICAL SALTS

Salt (0.002 *N*)	KCl	$MgCl_2$	$Ba(NO_3)_2$	Tl_2SO_4	$La(NO_3)_3$	$K_4Fe(CN)_6$
Conductance ratio, Λ/Λ_0	0.971	0.939	0.934	0.924	0.904	0.859
Ionic strength, μ	0.002	0.003	0.003	0.003	0.004	0.005

The dissociation of higher valence types of solutes is further complicated by the dissociation in stages giving rise to intermediate ions. For example, a bivalent salt such as calcium chloride can dissociate in the following manner:

$$(a)\ CaCl_2 \rightleftarrows CaCl^+ + Cl^-,$$
$$(b)\ CaCl^+ \rightleftarrows Ca^{++} + Cl^-.$$

* Z. physik. Chem., **33**, 545 (1900).

† Noyes and Coolidge, J. Am. Chem. Soc., **26**, 167 (1904).

At infinite dilution when ionization is complete, only two species of ions are present, but at finite concentrations there are three ionic species present in unknown relative amounts. Still further complications occur in concentrated solutions where the nature of the solvent itself is changed by the presence of the solute.

At one time it was thought that the influence of concentration on velocities of the ions could be corrected by the simple expedient of a viscosity correction as shown in the following equation,

$$\alpha = \frac{\Lambda}{\Lambda_0} \cdot \frac{\eta}{\eta_0} \tag{21}$$

where η and η_0 are the viscosities of the solution and solvent, respectively. Of late considerable doubt has been raised concerning the significance of this correction.

In the case of weak electrolytes the degree of dissociation, as determined by equation (20), checks well with the value obtained by the freezing-point method or related methods. Although it is true that there are examples of fairly close checks among the strong electrolytes, there are many cases where the agreement between the two methods is poor. Good agreement is not to be expected, because in the case of strong electrolytes equation (20) is a measure of the ratio of ionic velocities rather than a measure of the degree of dissociation. It will be remembered also that abnormal freezing-point depressions do not give a measure of the degree of dissociation. Furthermore, the equations used in the freezing-point methods are based on reversible processes, whereas the conductance measurements are essentially irreversible processes. In spite of these theoretical difficulties, the conductance ratio as given by equation (20) is used as a convenient method of estimating the extent to which the properties of an electrolyte differ from those at infinite dilution. It must be emphasized too that there is no sharp dividing line between weak electrolytes and strong electrolytes, and that there are boundary cases among strong electrolytes where the conductance ratio is in part a measure of the degree of dissociation.

Absolute Velocity of the Ions. Thus far we have considered only the relative velocities and conductances of uni-univalent ions; we now proceed to the consideration of their absolute velocities in centimeters per second.

Consider the passage of electricity through a centimeter cube of a solution of a uni-univalent electrolyte. The number of faradays carried across the cube in one second by the cations is equal to the product of the number of gram-equivalents contained in the cube by the ionic velocity of the cation in centimeters per second. A similar

relation holds for the anions. If the concentration of the electrolyte is C gram-equivalents per liter there will be $C/1000$ equivalents of each ion in the centimeter cube, provided that C is so small that the electrolyte is completely dissociated, and interionic attraction is negligible. Since the total quantity of electricity transported across a given section of a solution of an electrolyte by its ions is equal to the sum of the number of equivalents carried by the cations and the anions moving in opposite directions, it follows that the number of coulombs transported per second under unit potential gradient is

$$\left(\frac{C}{1000}\right)(U + V)\,F = I, \tag{22}$$

where U is the velocity of the cation for unit potential gradient, V the corresponding velocity of the anion, $F = 96{,}500$ coulombs, and I is the number of coulombs passing per second, or in other words the current in amperes. But by Ohm's law, $I = E/R = EL$, hence, equation (22) becomes

$$EL = \left(\frac{C}{1000}\right)(U + V)F, \tag{23}$$

or, for a potential gradient of 1 volt per centimeter,

$$L = \left(\frac{C}{1000}\right)(U + V)\,F. \tag{24}$$

Remembering that $\frac{C\Lambda}{1000} = L$, we have

$$\Lambda = (U + V)\,F. \tag{25}$$

By means of this equation, the velocities of the ions, expressed in centimeters per second, can be calculated, provided that the corresponding transference numbers are known. For example, the equivalent conductance of an 0.0001 molar solution of potassium chloride, at 18°, is 129; the total velocity of the two ions is then,

$$\frac{129}{96{,}500} = 0.00134 \text{ cm. per sec.}$$

This total velocity is made up of the two individual ionic velocities. The transference numbers of the two ions, K^+ and Cl^-, are respectively 0.496 and 0.504. Hence, the absolute velocities of the ions, expressed in centimeters per second, in an 0.0001 molar solution of potassium chloride, at 18°, are as follows:

$$U = 0.00134 \times 0.496 = 0.000665 \text{ cm. per sec.,}$$

and

$$V = 0.00134 \times 0.504 = 0.000675 \text{ cm. per sec.}$$

The absolute velocities of some of the more common ions, at 18°, are given in the following table.

ABSOLUTE IONIC VELOCITIES

Ion	Velocity cm. per sec.	Ion	Velocity cm. per sec.
K^+	0.00066	H^+	0.00320
NH_4^+	0.00066	Cl^-	0.00069
Na^+	0.00045	NO_3^-	0.00064
Li^+	0.00036	ClO_3^-	0.00057
Ag^+	0.00057	OH^-	0.00181
$Cr_2O_7^{--}$	0.000473	Cu^{++}	0.00031

The velocities of certain ions have been determined directly. Thus, the velocity of the hydrogen ions was measured by Lodge* in the following manner: — The tube *B*, Fig. 124, 40 centimeters long and 8 millimeters in diameter, was graduated and bent at right angles at the

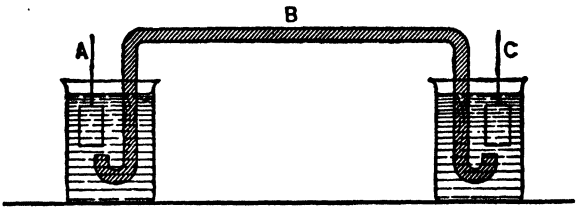


FIG. 124

ends. This was filled with an aqueous solution of sodium chloride in gelatine, colored red by the addition of an alkaline solution of phenolphthalein. When the contents of the tube had gelatinized, the tube was placed horizontally, connecting two beakers filled with dilute sulphuric acid, as shown in the diagram. A current of electricity was passed from one electrode *A* to the other electrode *C*. The hydrogen ions from the anode vessel traveled through the tube toward the cathode, causing the red color of the phenolphthalein to disappear. By observing the rate at which the color was discharged, the velocity of the hydrogen ion under a known potential gradient was determined. The observed and calculated values agree excellently. It was shown that the velocity of the hydrogen ion suffers almost no retardation from the high viscosity of the gelatine solution.

Whetham,† in his experiments on ionic velocity, employed two

* Brit. Assoc. Ann. Report, p. 393 (1886).

† Phil. Trans., **A 184**, 337 (1893); **196**, 507 (1895).

solutions, one of which possessed a colored ion, the motion of the latter being observed and its velocity determined under unit potential gradient. In this manner Whetham measured the absolute velocities of the ions, Cu^{++} and $Cr_2O_7^{--}$.

Ionic velocities have also been determined by Steele,* who observed the change in the index of refraction of the solution as the ions migrated. The accompanying table gives a comparison of the calculated and observed velocities of some of the ions.

ABSOLUTE IONIC VELOCITIES

Ion	Velocity (obs.) cm. per sec.	Velocity (calc.) cm. per sec.
H^+	0.0026	0.0032
Cu^{++}	0.00029	0.00031
Cl^-	0.00058	0.00069
$Cr_2O_7^{--}$	0.00047	0.000473

More recent work on the determination of moving boundaries has been done by MacInnes.†

Temperature Coefficient of Conductance. When the temperature of an aqueous solution of strong electrolytes is raised 1°, the equivalent conductance increases in the neighborhood of 2 per cent as shown in the following table. This increase is about the same as the decrease in viscosity, and the increased conduction is probably due to the greater velocity of the ions.

Kohlrausch suggested that each ion moving through the solution carries with it an atmosphere of solvent and that the frictional resistance offered to the motion of the ion is simply the frictional resistance between masses of pure water. This view is in harmony with other facts. According to this theory it would be expected that the most heavily hydrated ions would lose more of the water of hydration when heated and would have larger temperature coefficients of conductance. Many of the electrolytes shown in the lower part of the table are hydrated, as shown by the facts that they form crystals with water of crystallization and that they contain ions with small transport numbers. On the other hand, the electrolytes with small temperature coefficients at the head of the table contain hydrogen or hydroxyl ions.

The temperature coefficients generally increase with the temperature up to a maximum and then decrease as the critical temperature is ap-

* Phil. Trans., **A 198**, 105 (1902).

† J. Am. Chem. Soc., **45**, 2246 (1923); **47**, 1009 (1925).

proached,* owing possibly to a decrease in the dielectric constant of water. The increase with temperature of the conductance of weak electrolytes is due in part to an increase in the degree of dissociation.

TEMPERATURE COEFFICIENTS OF CONDUCTANCE

Electrolyte	$\frac{1}{\Lambda}\frac{\Delta\Lambda}{\Delta T}$ (room temperature)
Sulphuric acid	0 0164
Hydrochloric acid	0.0165
Potassium hydroxide	0.0190
Silver nitrate	0.0216
Potassium chloride	0.0217
Ammonium chloride	0.0219
Copper sulphate	0.0225
Sodium chloride	0.0226
Sodium sulphate	0.0234
Zinc sulphate	0.0250

The Conductance of Pure Liquids. In general, the conductance of pure liquids is small. Thus, the specific conductance of pure water, at 18°, is approximately 0.04×10^{-6} reciprocal ohm and, as Walden† has shown, the specific conductance of a number of other solvents is of the same order as that for water. Mixtures of two liquids, each of which is practically non-conducting, may have a conductance differing but little from that of the two components; or, the mixture may have a very high conductance. For example, the conductance of a mixture of water and ethyl alcohol is of the same order of magnitude as that of the two components; on the other hand, a mixture of water and sulphuric acid, each of which, in the pure state, is practically a non-conductor, has great conducting power. The variation of the specific conductance of mixtures of water and sulphuric acid is represented graphically in Fig. 125, concentration being plotted on the axis of abscissas and specific conductance on the axis of ordinates. It appears that as the concentration of the sulphuric acid increases, the specific conductance of the mixture increases until 30 per cent of acid is present, beyond which point it gradually diminishes. When pure sulphuric acid is present, the value of the specific conductance is practically zero. On dissolving sulphur trioxide in the pure acid, the specific conduc-

* Experiments were carried out by Noyes up to 306° in closed cells. Pub. Carnegie Inst. No. 63.

† Z. physik. Chem., **46**, 103 (1903).

tance increases slightly to a maximum, and then falls rapidly to zero. There is a minimum in the curve corresponding to about 85 per cent of acid, a concentration which corresponds almost exactly with the hydrate, $H_2SO_4 \cdot H_2O$. Many fused salts, such as silver nitrate and

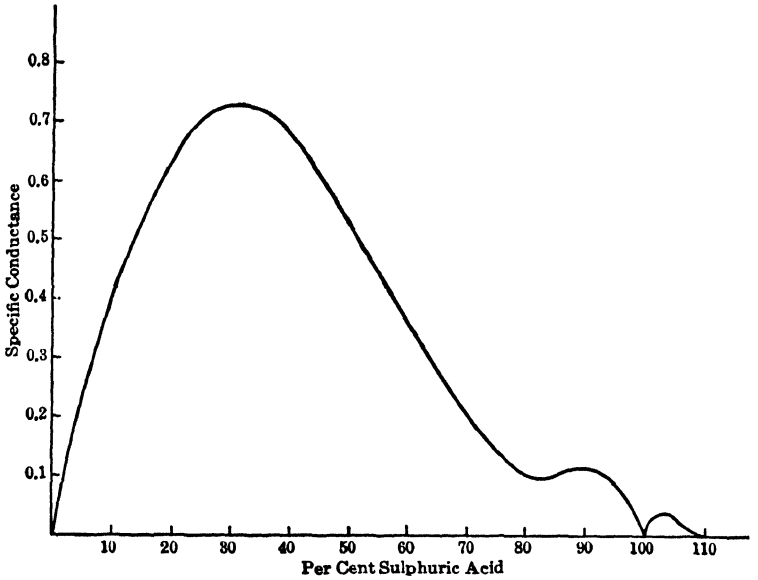


FIG. 125

lithium chloride, are excellent conductors and are thus exceptions to the general rule that pure substances are very poor electrolytic conductors.

Conductance of Fused Salts. While solid salts are exceedingly poor conductors of electricity, yet as the temperature is raised their conductance increases, until, at their melting-points, they become good conductors. The specific conductance of a fused salt may even exceed the specific conductance of the most concentrated aqueous solutions, but owing to its high concentration, the equivalent conductance is much less. The following table gives the specific and equivalent conductance of fused silver nitrate.

Temperature, degrees	Sp. Cond.	Equiv. Cond.
218 (melt.-pt.)	0.681	29.2
250	0.834	36.1
300	1.049	46.2
350	1.245	55.4

The specific conductance of a 60 per cent aqueous solution of silver nitrate, at 18°, is 0.208 reciprocal ohm.

If the salts are impure the conductance is raised, the effect of impurities being apparent even before the salts have reached their melting-points. This is analogous to the behavior of solutions, and suggests that the impurity functions in the salt mixture as a dissolved solute.*

Electrolysis in fused salts is a matter of great technical importance, notably in the production of metallic aluminum from bauxite in a bath of fused cryolite.

Conductance of Non-aqueous Solutions. A large amount of interesting work has been done in recent years on the electrical conductance of solutions in non-aqueous solvents. Some of this work is of technical importance. When the solvent is an inorganic or highly polar substance, such as ammonia, sulphur dioxide or hydrocyanic acid, the conductance is comparable with that of aqueous solutions, but when the solvent is an organic compound, the conductance is almost always very much less than that of the corresponding aqueous solution. The examples on p. 390 will serve to illustrate the wide variation in the conductance of solutions of silver nitrate in different solvents.

The conductance of alcoholic solutions is found to diminish as the molecular weight of the solvent increases. In fact, in any homologous series whose members form conducting solutions, the conductance decreases as the number of carbon atoms in the solvent increases.

A study of solutions in anhydrous formic acid has recently been made by Schlesinger,† who finds that these solutions are more nearly normal in their behavior than the corresponding aqueous solutions. Solutions of potassium iodide in acetone conduct better than the corresponding solutions in methyl and ethyl alcohols, whereas, the conductance of lithium chloride and silver nitrate in the latter solvents is much greater than in acetone. Solutions in pyridine are found to conduct well, while solutions in the analogous solvents, piperidine and quinoline, are to be classed among poor conductors. Such irregularities in the conductance of the same electrolyte in different non-aqueous solvents are found to be quite general.

In nearly every instance, the equivalent conductance increases with the dilution, as in the case of aqueous solutions. There are numerous exceptions to this rule, however, a notable example being that of sil-

* A complete treatment of fused electrolytes is given in "Die Elektrolyse geschmolzener Salze," by Richard Lorenz.

† J. Am. Chem. Soc., **41**, 1923 (1919).

CONDUCTANCE OF SILVER NITRATE IN DIFFERENT SOLVENTS*

Temp. 25°

Silver Nitrate in Ethyl Alcohol

c	$\Lambda_{25}°$
0.1	10.81
0.01	22.06
0.0078	23.72
0.003	28.14
0.001	34.95
0 00056	37.79
0.0003	38.52
0.0001	40.71

Silver Nitrate in Methyl Alcohol

c	$\Lambda_{25}°$
0.1	36.64
0.01	68.75
0.006	74.88
0.003	83.14
0 0012	87.30
0.001	90.10
0 0003	87.82
0 0001	73.23

Silver Nitrate in Acetone

c	$\Lambda_{25}°$
0.01	10 51
0.003	11 39
0.001	15 43
0 0003	20.78
0.00016	25 60
0.0001	28 06

Silver Nitrate in Aniline

c	$\Lambda_{25}°$
0 1	0.666
0 01	0.327
0 003	0.436
0 001	0.678
0.0003	1.082
0.0001	1.651

Silver Nitrate in Pyridine

c	$\Lambda_{25}°$
0.1	24 80
0.01	33 85
0.003	43 68
0.001	54 13
0 0003	66.14
0 0001	73 50
0.00006	75.82

* Gibbons and Getman, J. Am. Chem. Soc., **36**, 1640 (1914).

ver nitrate in aniline, the conductance curve of which is shown in Fig. 126.

The molecular weight of the solute in dilute aqueous solutions, as determined by the freezing-point and boiling-point methods, is usually much less than the simple formula-weight. In non-aqueous solutions, it is frequently greater.

Although solutions of electrolytes in the lower alcohols resemble aqueous solutions very closely, this resemblance is found to decrease rapidly as the molecular weight of the alcohol increases. Solutions of electrolytes in almost all other non-aqueous solvents do not appear to undergo dissociation in the same manner as in aqueous solutions. In fact, it is known that the molecules of electrolytes tend to become polymerized in non-aqueous solutions. These polymerized molecules

may be formed by the union of two or more molecules of the solute, or by the combination of one or more molecules of the solute with one or more molecules of the solvent. Undoubtedly, it is to the presence of such aggregates in certain non-aqueous solutions that the decrease in their conductance on dilution is to be ascribed. In those few cases

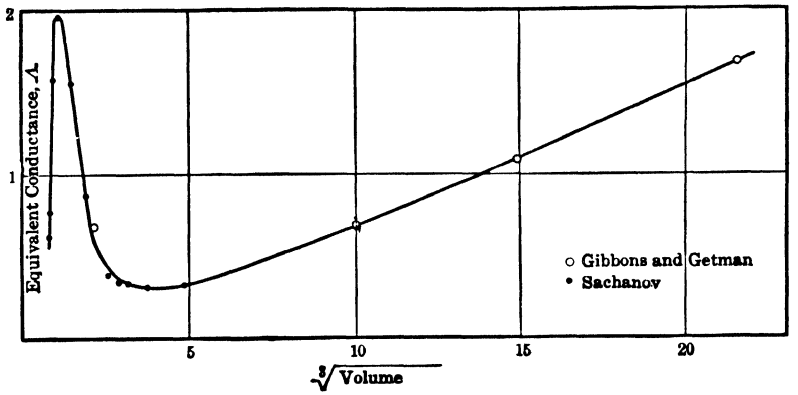


FIG. 126

where it has been possible to estimate the value of Λ_0, the degree of ionization, thus calculated, has rarely been found to agree with that calculated from freezing-point or boiling-point measurements.

New material on non-aqueous solutions has appeared recently.*

Ionizing Power of Solvents. Both Thomson† and Nernst‡ pointed out that, if the forces which hold the atoms in the molecule are of electrical origin, then those liquids which possess large dielectric constants should have correspondingly great ionizing power. This is a direct consequence of Coulomb's law of electrostatic attraction, which may be expressed by the equation,

$$f = \frac{q_1 q_2}{Dd^2}, \tag{26}$$

in which q_1 and q_2 denote the electric charges, d the distance between them, f the force of attraction and D the dielectric constant. Obviously the larger D becomes, the smaller will be the value of f; i.e., the more likely the molecule will be to break down into ions. That the above relation is approximately true may be seen from the following table.

* Evans, Chem. Rev., **8**, 167 (1931); Walden, "Salts, Acids and Bases."

† Phil. Mag. **36**, 320 (1893).

‡ Z. physik. Chem., **13**, 531 (1894).

DIELECTRIC CONSTANTS

Solvent	D	Solvent	D
Hydrocyanic acid	96.0	Ethanol	24.0
Water at 0°	88.2	Ammonia at −33.5°	22.0
Water at 25°	77.9	Acetone	21.2
Water at 100°	55.3	Pyridine	12.4
Formic acid	62.0	Ethyl ether	4.1
Nitrobenzene	34.2	Benzene	2.3
Methanol	30.3		

The dielectric constants are given at 25° unless otherwise designated. All the liquids with large dielectric constants have the ability to ionize polar solutes to a marked extent whereas the liquids with the lowest dielectric constants have very little ionizing power. There is only a rough parallelism between dielectric constants and ionizing power because chemical combination and other factors may also be involved. Dutoit and Aston* have suggested that there is a connection between the ionizing power of a solvent and its degree of association.

Applications of Conductance Measurements. (a) *The Dissociation of Water.* Water behaves as a very weak binary electrolyte, dissociating according to the equation,

$$H_2O \rightleftarrows H^+ + OH^-.$$

The specific conductance of water, purified with the utmost care, has been determined by Kohlrausch and Heydweiller.† Their results are given in the following table:

SPECIFIC CONDUCTANCE OF WATER

Temperature, degrees	Specific Conductance $\times 10^6$
0	0.014
18	0.040
25	0.055
34	0.084
50	0.170

The conductance of pure water, at 0°, is so small that 1 millimeter of it has a resistance equal to that of a copper wire of the same cross

* Compt. rend., **125**, 240 (1897).

† Z. physik. Chem., **14**, 317 (1894).

section and 40,000,000 kilometers in length, or in other words, long enough to encircle the earth one thousand times. Knowing the specific conductance of water, its degree of dissociation can easily be calculated. The ionic conductances of the two ions of water, at 18°, are as follows: $H^+ = 315$, and $OH^- = 174$. Therefore, the maximum equivalent conductance of water should be,

$$\Lambda_0 = 315 + 174 = 489.$$

The equivalent conductance, at 18°, of water is, according to the data of Kohlrausch,

$$0.04 \times 10^{-6} \times 18 = 0.72 \times 10^{-6},$$

where 18 is the volume in cc. holding one equivalent. Therefore, by equation (20)

$$\frac{0.72 \times 10^{-6}}{489} = 0.147 \times 10^{-8} = \alpha \text{ (the degree of dissociation).}$$

Since there are 55.5 mols of water per liter, $55.5\,\alpha$ = the concentration of H^+ and OH^- ions in gram-equivalents per liter = 0.82×10^{-7}.

(b) *Solubility of Difficultly Soluble Salts.* In a saturated solution of a difficultly soluble salt, the solution is so dilute that, in general, we may assume complete ionization, or $\Lambda = \Lambda_0$.

When this is the case, we have

$$L_{\text{solution}} - L_{H_2O} = L, \tag{27}$$

and

$$\Lambda = \Lambda_0 = \frac{1000\,L}{C}. \tag{28}$$

Hence,

$$C = \frac{1000\,L}{\Lambda_0}, \tag{29}$$

where C denotes the concentration in gram-equivalents per liter. Thus, Böttger found for a saturated solution of silver chloride, at 20°, $L' = 1.374 \times 10^{-6}$. Deducting the specific conductance of the water at this temperature, we have

$$L = 1.374 \times 10^{-6} - 0.044 \times 10^{-6} = 1.33 \times 10^{-6}.$$

Since the value of Λ_0, at 20°, for silver chloride, determined from the table of ionic conductances, is 119, we have

$$C = \frac{1000 \times 1.33 \times 10^{-6}}{119} = 1.12 \times 10^{-5} \text{ gr.-equiv. AgCl per liter.}$$

(c) *The Basicity of Organic Acids.* The difference in conductance between two dilutions of a neutral salt of a polybasic acid is greater

than the difference in conductance between the same dilutions of a neutral salt of a monobasic acid.

Ostwald* has shown that it is possible to estimate the basicity of an organic acid from the difference in the equivalent conductance of its sodium salt at two different dilutions. As the result of a long series of experiments, he found empirically that the difference between the molar conductance of the sodium salt of a monobasic organic acid, at $v = 32$ liters, and at $v = 1024$ liters, is approximately 10 units. Similarly, for a dibasic acid, the difference between the same dilutions is 20 units, and for an n-basic acid the difference is $10\,n$. Hence, to estimate the basicity of an organic acid, the molar conductance of its sodium salt, at $v = 32$ liters, and at $v = 1024$ liters, is determined; then, if Δ is the difference between the values of the conductance at the two dilutions, the basicity will be $n = \Delta/10$.

The following table gives the values of Δ and n for the sodium salts of several typical organic acids.

BASICITY OF ORGANIC ACIDS

Acid	Δ	n
Formic	10.3	1
Acetic	9.5	1
Propionic	10.2	1
Benzoic	8.3	1
Quininic	19.8	2
Pyridine-tricarboxylic (1, 2, 3)	31.0	3
Pyridine-tricarboxylic (1, 2, 4)	29.4	3
Pyridine-tetracarboxylic	41.8	4
Pyridine-pentacarboxylic	50.1	5

(d) *Determination of Hydrolysis.* The degree of hydrolysis (defined on p. 412) can be determined experimentally in several different ways. A very convenient method is that based upon measurements of electrical conductance. When a salt reacts hydrolytically with 1 mol of water, the limiting value of its equivalent conductance will be $\Lambda_A + \Lambda_B$, where Λ_A and Λ_B denote the equivalent conductances of the acid and base formed. If Λ is the equivalent conductance of the unhydrolyzed salt, and Λ_h is the actual conductance of the salt at the same dilution, then the increase in conductance, corresponding to a degree of hydrolysis, x, will be $\Lambda_h - \Lambda$. If the hydrolysis were complete, the

* Z. physik. Chem., **1**, 105 (1887); **2**, 902 (1888).

increase in equivalent conductance would be $\Lambda_A + \Lambda_B - \Lambda$, hence we have

$$x = \frac{\Lambda_h - \Lambda}{\Lambda_A + \Lambda_B - \Lambda}, \tag{30}$$

all conductances being measured at the same dilution and at the same temperature. The value of Λ may be found by determining the conductance of the salt in the presence of an excess of one of the products of hydrolysis, and deducting from it the conductance of the substance added.

The following example illustrates the use of this equation: — At 25°, the equivalent conductance of an aqueous solution of aniline hydrochloride is 118.6, the dilution being 99.2 liters. The equivalent conductance, in the presence of an excess of aniline, is 103.6; the equivalent conductance of hydrochloric acid, at the same dilution, is 381. The conductance of pure aniline is so small as to be negligible. Substituting these values in the above equation, we find

$$x = \frac{118.6 - 103.6}{381 - 103.6} = 0.0541.$$

(e) *Determination of End-points.* The possibility of determining the end-points in titration reactions by means of the conductance method was first pointed out by Kohlrausch* in 1885. Subsequent research by numerous investigators† has demonstrated the applicability of the method to a wide variety of reactions.

The conductance of a solution being dependent upon both the concentration and the speed of its ions, it follows that any changes which may occur in either of these factors during a reaction will produce corresponding changes in the electrical conductance of the reaction mixture. In the case of the neutralization of a strong acid by a strong base, the conductance of the acid will diminish as its highly mobile hydrogen ions are gradually replaced by the slower moving cations of the base. Since the degree of ionization of the resulting salt is of the same order of magnitude as that of the acid, it follows that the conductance of the acid solution will continue to decrease until the end-point is reached and all the hydrogen ions have combined with the hydroxyl ions of the base. As soon as an excess of the base is added, however, the conductance will begin to increase cor-

* Ann. physik. Chem., **26**, 225 (1885).

† Küster, Grüters and Geibel, Z. anorg. Chem., **42**, 225 (1904); Dutoit, J. chim. phys., **8**, 12 (1910); Kolthoff, Z. anal. Chem., **61**, 171, 229, 332, 369, 433 (1922); **62**, 1, 97, 161, 209 (1923).

responding to the increase in the total number of ions, especially to the increase in the number of fast-moving hydroxyl ions.

A typical experiment is shown in Fig. 127 where the conductances are plotted against the cubic centimeters of base added to a given acid. The abscissa corresponding to the point B at which the two lines intersect is the end-point. In order that AB and BC shall be straight lines it is necessary to keep the volume constant throughout the titration. This condition is fulfilled in practice if the total volume of the reagent is not more than 2 per cent of the volume of the solution to be titrated. In other words, the reagent must be concentrated whereas the solution which is being titrated must be dilute. If these conditions are fulfilled, four readings corresponding to the points A, D, E and C suffice to determine the end-point in the titration of a strong acid by a strong base.

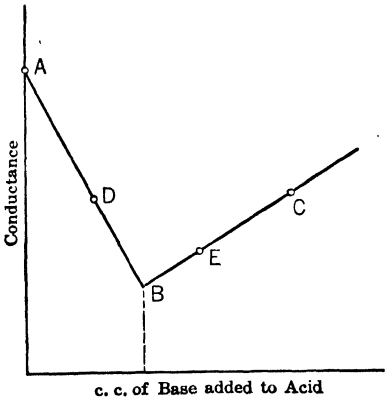


FIG. 127

If the base is weak, the line BC is more nearly horizontal and the lines do not meet at such a sharp angle because, after the rapidly moving hydrogen ions are converted into water molecules, the conductance is small and the excess base does not contribute many hydroxyl ions inasmuch as it is only slightly ionized. This type of titration gives somewhat less accurate results.*

In practical work it is usually more convenient to plot resistance or merely bridge readings instead of conductances against the burette readings.

Conductimetric titrations have proved of great value in titrating colored or turbid solutions in which the determination of the end-point is often rendered uncertain owing to the masking of the indicator by the color of the solution.

The conductance method may also be applied to the determination of the end-points of reactions involving precipitations; in fact, the method is often superior to the more familiar analytical procedures. It has been used, for example, in the precipitation of silver iodide, barium sulphate, and uranium sulphate.† One of the best reactions

* Similar titrations of polybasic acids and mixtures of acids are discussed by Kolthoff, Z. anorg. Chem., **111**, 1, 28, 97 (1920); **112**, 155, 196 (1921); Ind. Eng. Chem., Analyt. Ed., **2**, 225 (1930).

† Van Suchtelen and Itano, J. Am. Chem. Soc., **36**, 1793 (1914).

for this method is the precipitation of a bivalent metal sulphate with barium hydroxide,* for in this case both the products are insoluble and the conductance at the end-point is very low. Titration curves are obtained for precipitation reactions similar to the neutralization reaction shown in Fig. 127 when there is a marked change in conductance on precipitation.

REFERENCES

Electrochemistry, Vol. I, Chapter V. Creighton and Fink.
The Conductivity of Solutions. Davies.
Treatise on Physical Chemistry, Chapter XI. Taylor.
The Properties of Electrically Conducting Systems. Kraus.
Applied Electrochemistry, Chapter I. Thompson.
Electrochemistry of Solutions. Glasstone.
Electrolytic Conduction. Newman.

PROBLEMS

1. A uniform current drawn from a 6 volt battery deposited 0.2348 g. of silver from a silver nitrate solution in 35 minutes. (*a*) How many coulombs of electricity flowed through the circuit? (*b*) What was the current? (*c*) How much energy was consumed? *Ans.* (*c*) 1260 joules.

2. The resistance of a certain electric light bulb is 302.5 ohms. (*a*) How much current in amperes flows through the lamp when it is connected to a 110 volt circuit? (*b*) What is the wattage of the lamp? (*c*) At 3 cents a kilowatt-hour how much does it cost to operate the lamp continuously for a week?

3. (*a*) How much silver will a current of 0.2 ampere deposit in one hour? (*b*) How many atoms? (*c*) How much iodine will it liberate in 50 minutes?

Ans. (*a*) 0.8050 g.

4. A uniform current deposits 0.6332 g. of silver in 90 minutes. (*a*) What volume of hydrogen at 25° and 740 mm., measured over water (vapor pressure at 25° = 23.7 mm.) would it liberate in one hour? (*b*) How long would it take this current to deposit a gram of copper?

5. A solution of hydrochloric acid was electrolyzed in a transference cell between platinum electrodes. The cathode compartment contained 0.177 g. of chloride ions before the electrolysis and 0.163 g. after. A silver coulometer in series had a deposit of silver equivalent to 0.0825 g. of chloride ions. What are the transference numbers of H^+ and Cl^-?

6. An aqueous solution of copper sulphate is electrolyzed between copper electrodes until 0.2294 g. of copper is deposited. Before electrolysis the solution at the anode contained 1.1950 g. of copper, after electrolysis 1.3600 g. Calculate the transference numbers of the two ions, Cu^{++} and SO_4^{--}.

Ans. 0.72 for sulphate ion.

7. A solution containing 0.1605 per cent of sodium hydroxide was electrolyzed between platinum electrodes. After electrolysis 55.25 g. of the cathode solution contained 0.09473 g. of sodium hydroxide, while the concentration of the middle portion of the electrolyte was unchanged. In a silver coulometer the equivalent of

* Harned, J. Am. Chem. Soc., **39**, 252 (1917).

0.0290 g. of NaOH was deposited during electrolysis. Calculate the transference numbers of the Na^+ and OH^- ions.

8. The silver nitrate solution from the central compartment of a transference cell weighed 36.5 g. and was titrated with 32.7 cc. of ammonium thiocyanate solution, one cc. of which was equivalent to 0.0085 g. of silver nitrate. The solution from the cathode compartment weighed 43.17 g. and required 29.4 cc. of ammonium thiocyanate solution. A silver coulometer in series with the transference cell had a deposit of 0.0994 g. of silver. What are the transference numbers of the silver ion and the nitrate ion?

9. A certain conductance cell gave a resistance of 74.1 ohms when containing 0.02 *M* KCl and 349 ohms when containing 0.0025 *M* Na_2SO_4. The temperature was 25° C. What is the cell constant? What are the values of the equivalent and molar conductances of Na_2SO_4? *Ans.* $\mu = 234.5$ reciprocal ohms.

10. In a 0.01 molar solution of potassium nitrate, the transference numbers of the cation and anion are, respectively, 0.503 and 0.497. Find the equivalent conductances of the two ions in this solution, having given that its specific conductance is 0.001044. *Ans.* $l_c = 52.5$, $l_a = 51.9$.

11. A 0.02 molar solution of ammonium iodate has a specific conductance of 0.001962 reciprocal ohms. The transference numbers are $n_c = 0.656$ and $n_a = 0.344$. What are the ionic conductivities of NH_4^+ and IO_3^-?

12. At 25° Λ_0 for lithium chloride is 114. $n_a = 0.66$ and $n_c = 0.34$. What are the absolute ionic velocities of Li^+ and Cl^- at 25° under a unit potential gradient? What are the ionic velocities in a cell with electrodes 4 cms. apart having across it a potential of 6 volts?

13. The equivalent conductance of an infinitely dilute solution of ammonium chloride is 130; the ionic conductances of the ions, OH^- and Cl^-, are 174 and 65.4 respectively. Calculate the equivalent conductance of ammonium hydroxide at infinite dilution. *Ans.* $\Lambda_0 = 238.6$.

14. The absolute velocity of the Ag^+ ion is 0.00057 cm. per sec., and that of the Cl^- ion is 0.00069 cm. per sec. Calculate the equivalent conductance of an infinitely dilute solution of silver chloride.

15. At 25° the equivalent conductance of sodium acetate at infinite dilution is 91.3. The conductances of Na^+ and H^+ are 50.5 and 350 respectively. What is the equivalent conductance of an infinitely dilute solution of acetic acid at 25°?

16. At 25° C. the equivalent conductance at infinite dilution Λ_0 of chloracetic acid is 389. Using the table of ionic conductances and temperature coefficients on p. 379, calculate Λ_0 at 25° for sodium chloracetate.

17. A conductance cell at 18° had a resistance of 35.16 ohms when containing 0.02 *M* KCl and 179 ohms when containing 0.1 *M* acetic acid. What is the degree of ionization of the acetic acid? For acetic acid, $\Lambda_0 = 350$.

18. From the data given in the table on page 377 determine Λ_0 for NaCl by plotting $1/\Lambda$ against $\sqrt{C\Lambda}$ and extrapolating the best straight line, through the points, to the axis where $\sqrt{C\Lambda}$ is zero.

19. The specific conductance of a saturated solution of silver cyanide at 20° is 1.79×10^{-6} and the specific conductance of water at the same temperature is 0.044×10^{-6} reciprocal ohms. The equivalent conductance at infinite dilution is 115.5. Calculate the solubility of silver cyanide in grams per liter.

Ans. 0.00202 g. per liter.

20. The specific conductance of a saturated solution of silver chloride at 25° is $3.1 \cdot 10^{-6}$ and the specific conductance of the water used was $1.3 \cdot 10^{-6}$ reciprocal

ohms. The equivalent conductance of AgCl at infinite dilution is 137.5. What is the solubility of AgCl at 25°?

21. The specific conductance at 25° of a saturated solution of barium sulphate was $4.58 \cdot 10^{-6}$ reciprocal ohms and that of the water used was $1.52 \cdot 10^{-6}$. The equivalent conductance at infinite dilution of barium sulphate is 143. What is the solubility of $BaSO_4$ at 25° in (*a*) gram-equivalents per liter, (*b*) mols per liter, and (*c*) grams per liter?

22. The equivalent conductance of aniline hydrochloride at a dilution of 197.6 liters is 126.7 reciprocal ohms, at 25°. The equivalent conductance of aniline hydrochloride in the presence of an excess of aniline is 106.6; and the equivalent conductance of hydrochloric acid at the same dilution is 415. If the conductance of pure aniline is negligible, calculate the degree of hydrolysis.

Ans. 6.52 per cent.

23. The following table gives the specific conductance of a solution of hydrochloric acid, to 100 cc. of which have been added various amounts of an 8.*N* solution of sodium hydroxide. Neglecting the dilution effect of the small amount of hydroxide solution added, what is the normality of the hydrochloric acid solution?

cc. NaOH	0.32	0.92	1.56	2.34
conductance	0.0322	0.0186	0.0164	0.0296

24. We have seen α expressed as $\alpha = \frac{i-1}{n-1}$ $\left(\text{or } \frac{\nu g - 1}{\nu - 1}\right)$ (p. 197) and as $\alpha = \frac{\Lambda}{\Lambda_0}$ (p. 381). The former is determined under static, or equilibrium conditions; the latter under dynamic conditions. Denote these by α_s and α_d respectively and determine their values for 0.1 *m* $MgSO_4$ from the following data:

Freezing-point of 0.1 *m* $MgSO_4 = -.225°$ C.
Λ for 0.1 *m* $MgSO_4$ at 0° = 26.5.
Λ_0 for $MgSO_4$ at 0° = 64.

It will be noted that the agreement is not within the limits of experimental error, indicating that there is a fundamental difference between the two methods, and that α cannot be interpreted simply as a "degree of dissociation."

CHAPTER XVI

ELECTROLYTIC EQUILIBRIUM AND HYDROLYSIS

Ostwald's Dilution Law. It has been shown, in preceding chapters, that the law of mass action is applicable to chemical equilibria, in both gaseous and liquid systems. We now proceed to show that it applies equally to electrolytic equilibria. When acetic acid is dissolved in water it dissociates according to the equation,

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+.$$

Let 1 mol of acetic acid be dissolved in water, and the solution diluted to v liters, and let α denote the degree of dissociation. Then, the concentration of the undissociated acid is $(1 - \alpha)/v$, and the concentration of each of the ions is α/v.

The equilibrium or ionization constant, K, is given by the following expression,

$$K = \frac{c_{H^+} \times c_{CH_3COO^-}}{c_{CH_3COOH}} = \frac{\frac{\alpha}{v} \times \frac{\alpha}{v}}{\frac{1 - \alpha}{v}} = \frac{\alpha^2}{(1 - \alpha)v}. \qquad (1)$$

This equation, expressing the relation between the degree of ionization and dilution, was derived by Ostwald,* and is known as the Ostwald dilution law. For an electrolyte which forms more than two ions the mathematical form of the law will be different. The dilution law may be tested by substituting the value of α, corresponding to any dilution v, in equation (1) and calculating the value of the ionization constant, K; the value of α, at any other dilution, may then be calculated, and compared with the value determined by direct experiment. The following table gives the results obtained with acetic acid at 14.1°. Here K has the value, 0.0000178, and α is obtained from conductance measurements, as given by equation (20) of the preceding chapter.

As will be seen, the agreement between the observed and calculated values is very close. The table also shows to how small an extent the molecules of acetic acid are broken down into ions, a molar solution

* Z. physik. Chem., **2**, 36 (1888); **3**, 170 (1889).

being dissociated less than 0.5 per cent. The dilution law holds for nearly all organic acids and bases, but fails to apply to salts, strong

DEGREE OF IONIZATION OF ACETIC ACID

v (in liters)	$\alpha \times 10^2$ (calc.)	$\alpha \times 10^2$ (obs.)
0.994	0.42	0.40
2.02	0.60	0.614
15.9	1.67	1.66
18 1	1 78	1.78
1,500.0	15.0	14 7
3,010.0	20.2	20.5
7,480.0	30 5	30.1
15,000.0	40.1	40 8

acids, and strong bases. When α is small, the term $(1 - \alpha)$ does not differ appreciably from unity, and equation (1) becomes,

$$\frac{\alpha^2}{v} = K, \tag{2}$$

or

$$\alpha = \sqrt{vK}. \tag{3}$$

On the other hand, when α cannot be neglected, we have, on solving equation (1) for α,

$$\alpha = -\frac{vK}{2} + \sqrt{vK + \frac{v^2K^2}{4}}. \tag{4}$$

It has been found that organic acids, whether they are mono-, di-, or polybasic, always ionize as a monobasic acid up to the dilution at which the acid is about half ionized, and that equation (1) is applicable up to such a dilution.

It is generally true that the first hydrogen ionizes from an acid (or the first hydroxyl ionizes from a base) much more easily than a second one. Thus in the ionization of carbonic acid

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad K = 3 \times 10^{-7},$$
$$HCO_3^- \rightleftarrows H^+ + CO_3^{--} \qquad K = 6 \times 10^{-11}.$$

The larger constant shows that carbonic acid dissociates to give hydrogen ions and bicarbonate ions much more readily than bicarbonate ions dissociate into hydrogen ions and carbonate ions.

Strengths of Acids and Bases. Acid properties in aqueous solutions are attributed chiefly to hydrogen ions, and basic properties chiefly to hydroxyl ions. Strong acids are those like hydrochloric acid which are

largely dissociated into hydrogen ions; weak acids are those like acetic acid which are only slightly dissociated. The terms *concentrated* and *dilute* have reference to the number of mols per unit of solvent without reference to the extent of the dissociation. Both strong and weak acids and bases may exist in either concentrated or dilute solutions.

The following table gives the values of the ionization constants at 25° for several different acids.

IONIZATION CONSTANTS OF ACIDS

Acid	Ionization Constant
Hydrochloric	10^{5} to 10^{7}
Iodic	2×10^{-1}
Dichloracetic	5.2×10^{-2}
Chloracetic	1.5×10^{-3}
Formic	2.1×10^{-4}
Acetic	1.8×10^{-5}
Carbonic K_1	3×10^{-7}
K_2	6×10^{-11}
Boric K_1	7×10^{-10}
K_2	2×10^{-13}
K_3	2×10^{-14}

Since for a weak acid $\alpha = \sqrt{vK}$, it follows that, for two weak acids at the same dilution, we may write,

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}, \tag{5}$$

or, the ratio of the degrees of ionization of the two acids is equal to the square root of the ratio of their ionization constants. Thus, from the data given in the foregoing table for acetic and monochloracetic acids, we have

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{0.000018}{0.00155}} = \frac{1}{9.3},$$

or, the effect of replacing one atom of hydrogen by an atom of chlorine in the methyl group in acetic acid increases the strength of the acid about nine times.

Just as the hydrogen ion concentration of acids determines their strength, so the strength of bases is determined by the concentration of hydroxyl ions. The strength of bases may be estimated by methods similar to those employed in determining the strength of acids. A catalytic method, developed by Koelichen,* is based upon the effect

* Z. physik. Chem., **33**, 129 (1900).

of hydroxyl ions on the rate of condensation of acetone to diacetonyl alcohol, as represented by the equation,

$$2\,CH_3COCH_3 = CH_3COCH_2C(CH_3)_2OH.$$

In addition to these two methods, the method of electrical conductance is also applicable. The agreement between the results obtained by the three methods is quite satisfactory. The alkali and alkaline earth hydroxides are very strong bases, and are dissociated to about the same extent as equivalent solutions of hydrochloric and nitric acids, while on the other hand, ammonia and many of the organic bases are very weak. The following table gives the ionization constants of several typical bases.

IONIZATION CONSTANTS OF BASES

Base	Ionization Constant
Ammonia	0.000018
Methylamine	0.00040
Trimethylamine	0.000062
Pyridine	1.6×10^{-9}
Aniline	4.2×10^{-10}

Influence of Substitution on Ionization. Attention has already been called to the marked difference in the strength of acetic acid produced by the replacement of the hydrogen atoms of the methyl group by chlorine. In the accompanying table the ionization constants for various substitution products of acetic acid are given.

IONIZATION CONSTANTS OF SUBSTITUTED ACETIC ACIDS

Acid	Ionization Constant (25°)
Acetic, CH_3COOH	0.000018
Propionic, CH_3CH_2COOH	0.000013
Chloracetic, $CH_2ClCOOH$	0.00155
Bromacetic, $CH_2BrCOOH$	0.00138
Cyanacetic, $CH_2CNCOOH$	0.00370
Glycollic, $CH_2OHCOOH$	0.000152
Phenylacetic, $C_6H_5CH_2COOH$	0.000056

This table affords an interesting illustration of the influence of different substituents on the strength of acetic acid. Thus, the strength of the acid is increased by the replacement of alkyl hydro-

gen atoms by Cl, Br, CN, OH, or C_6H_5, while the substitution of the CH_3 group diminishes its strength. If we assume that the substituents retain their ion-forming capacity on entering into the molecule of acetic acid, these differences in strength can be readily explained. Thus, Cl, Br, CN, and OH tend to form negative ions, and hence increase the negative character of the group into which they enter.

The influence of an alkyl residue on the strength of an organic acid is conditioned by its distance from the carboxyl group. This is well illustrated by the ionization constants of propionic acid and some of its derivatives. The effect of the OH group, in the α-position, is seen to be much more marked than when it occupies the β-position.

IONIZATION CONSTANTS OF PROPIONIC ACID DERIVATIVES

Acid	Ionization Constant (25°)
Propionic acid, CH_3CH_2COOH	0.0000134
Lactic acid, $CH_3CHOHCOOH$	0.000138
β-hydroxypropionic acid, CH_2OHCH_2COOH	0.0000311

The position of a substituent in the benzene nucleus exerts a marked influence on the strength of the derivatives of benzoic acid. The ionization constants of benzoic acid, and the three chlorbenzoic acids are given in the following table.

IONIZATION CONSTANTS OF BENZOIC ACID DERIVATIVES

Acid	Ionization Constant (25°)
Benzoic acid, C_6H_5COOH	0.000073
o-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.00132
m-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.000155
p-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.000093

When the halogen enters the ortho-position, the strength of the acid is greatly augmented, while in the meta- and para-positions, the effect is much smaller, meta-chlorbenzoic acid being stronger than para-chlorbenzoic acid. It is a general rule that the influence of substituents is always greatest in the ortho-position, and least in the meta- and para-positions, the order in the two latter being uncertain.

Proton Theory of Acids and Bases. Our view of acids and bases and neutralizations has been limited by our emphasis on water solutions.

We have come to think of neutralization only in terms of hydrogen and hydroxyl ions, but as a matter of fact the formation of water is neither a necessary nor a sufficient criterion for a neutralization reaction. For example, in benzene solution the reaction between hydrochloric acid and ammonia is a typical neutralization, which gives the usual neutralization curve with electrometric titration. The reaction is

$$HCl + NH_3 = NH_4Cl \text{ (in benzene)}.$$

Another typical neutralization is given by the equation

$$HCl + NaC_2H_3O_2 = HC_2H_3O_2 + NaCl \text{ (in glacial acetic acid)}.$$

Hydroxyl ions (OH^-) have particular significance only when water is used as a solvent, and then *hydrolysis* becomes important.

Franklin and Kraus and their co-workers have pointed out repeatedly that, when liquid ammonia is used as a solvent, the NH_2^- ions are important in reactions with the solvent as shown by the equation

$$NH_3 = NH_2^- + H^+,$$

and that the hydroxyl ions are without special significance. Ammonolysis occurs instead of hydrolysis.

Also, when acetic acid is the solvent the acetate ions become important.

The one reaction common to all these cases is simply the transfer of a hydrogen ion or proton (Chapter XXIII), and in the hands of Brönsted and others, the *proton theory* of acids and bases has been developed to give a new view of neutralization which has led to productive advances in several fields.* According to this theory an acid A is something which gives up protons (hydrogen ions), and a base B is a substance which combines with protons. For example, in the reaction

$$A \rightleftarrows H^+ + B$$

the acid dissociates to give hydrogen ions and a base. Further applications of the theory lead through logical steps to definitions which appear somewhat radical at first sight but which offer certain advantages. A few illustrations are given below.

$$HAc \rightleftarrows H^+ + Ac^-$$
$$NH_4^+ \rightleftarrows H^+ + NH_3$$
$$H_2O \rightleftarrows H^+ + OH^-$$
$$H_3O^+ \rightleftarrows H^+ + H_2O$$
$$HSO_4^- \rightleftarrows H^+ + SO_4^=.$$

* This subject is discussed clearly by N. F. Hall, J. Chem. Educ., **7**, 782 (1930); Chem. Rev., **8**, 191 (1931).

According to this convention, all the substances at the left in these equations may be called acids and all the substances at the extreme right may be called bases. Both A and B may have any number of charges or none, but A must be one unit more positive than B for a given reaction.

Neutralizations, then, are reactions which involve the transfer of protons in the same way that oxidations involve the transfer of electrons, as described in the following chapter.

The hydronium ion $H^+ \cdot nH_2O$ or H_3O^+ is the hydrated hydrogen ion. It is very common; in fact, free protons or unattached hydrogen ions can scarcely exist in the neighborhood of polar molecules, for they have a great tendency to become solvated.

The apparent strength of an acid in different solvents is inversely proportional to its dissociation, because the strength depends on the looseness with which the proton is bound either to the acid anion or to the solvent molecules (as in H_3O^+). In a non-basic solvent like benzene an acid may be *strong* because the proton is weakly held by the acid anion, and it will be *undissociated* because the solvent cannot take the proton away and permit the reaction of dissociation to occur. Thus, in the following equation where HX represents an acid and S a solvent,

$$HX + S \rightleftarrows HS^+ + X^-.$$

In a more basic solvent like water the same acid may be completely dissociated, but will be weaker because the very fact that the dissociation has occurred shows that the proton is more firmly bound in H_3O^+ than in HX.

Of course different acids in the *same solvent* will be dissociated in proportion to their strengths, and all acids above a certain strength may be completely dissociated.

Mixtures of Two Electrolytes with a Common Ion. Just as the dissociation of a gaseous substance is diminished by the addition of an excess of one of the products of dissociation, so the ionization of weak acids and bases is depressed by the addition of a salt having an ion common to the acid or the base. If the degree of ionization of a salt having an ion in common with an acid or a base is represented by α', and if c denotes the concentration of the salt in mols per liter, then the equation of equilibrium of the acid or base will be

$$\left(c\alpha' + \frac{\alpha}{v}\right)\alpha = K\ (1 - \alpha), \tag{6}$$

where α is the degree of ionization of the acid or base. For very weak

acids and bases, α is so small that α/v is negligible in comparison with $c\alpha'$ and that $1 - \alpha$ does not differ appreciably from unity, and since α' is practically independent of the dilution and can be incorporated in the constant K', we obtain

$$c\alpha = K', \tag{7}$$

or

$$\alpha = \frac{K'}{c}. \tag{8}$$

That is, the degree of ionization of a weak acid or base, in the presence of one of its salts, is approximately inversely proportional to the amount of salt present and is independent of the concentration of the acid.

In many of the processes of analytical chemistry, advantage is taken of the action of neutral salts on the ionization of weak acids and bases. Thus, whereas the concentration of hydroxyl ions in ammonium hydroxide is sufficient to precipitate magnesium hydroxide from solutions of magnesium salts, the presence of a small amount of ammonium chloride depresses the ionization of the ammonium hydroxide to such an extent that precipitation no longer takes place. These relations can be expressed more satisfactorily in terms of the solubility product.

The Solubility Product. While the law of concentration effect does not, in general, apply to the equilibrium between the dissociated and undissociated portions of an electrolyte — except in the case of weak acids and bases — it does apply with a fair degree of accuracy to saturated solutions of difficultly soluble salts, especially because such solutions are exceedingly dilute.

A saturated solution of silver chloride affords an example of such an equilibrium. This salt is practically completely ionized in a saturated solution, as represented by the equation,

$$AgCl \rightleftarrows Ag^+ + Cl^-.$$

Applying the law of mass action to this equilibrium, we obtain

$$\frac{c_{Ag^+} \times c_{Cl^-}}{c_{AgCl}} = K.$$

Since the solution is saturated, the value of c_{AgCl} must remain constant at constant temperature, and therefore,

$$c_{Ag^+} \times c_{Cl^-} = \text{constant} = s, \tag{9}$$

where the product of the ionic concentrations, s, is called the *solubility product.*

The equilibria in the above heterogeneous system may be represented thus,

$$Ag^+ + Cl^- \rightleftarrows \underset{\text{(in solution)}}{AgCl} \rightleftarrows \underset{\text{(solid)}}{AgCl}.$$

The solubility of silver chloride in pure water, at 25°, is 1.25×10^{-5} mol per liter, and since the dissociation is complete, there must be 1.25×10^{-5} gram-ion of Ag^+ and 1.25×10^{-5} gram-ion of Cl^- per liter. The solubility product s is therefore $(1.25 \times 10^{-5})^2$, or 1.56×10^{-10}.

In general, if

$$nA \rightleftarrows n_1A_1 + n_2A_2$$

represents the equilibrium between an electrolyte and its products of dissociation in saturated solution, we have

$$c^{n_1}{}_{A_1} \cdot c^{n_2}{}_{A_2} = s. \tag{10}$$

The solubility product may be defined as the maximum product of the ionic concentrations of an electrolyte which can exist in equilibrium with the undissolved phase at any one temperature, each concentration being raised to its proper power.

Just as the dissociation of a gaseous substance, or of an organic acid, is depressed by the addition of one of the products of dissociation, so when a substance with a common ion is added to the saturated solution of a slightly soluble electrolyte, the dissociation is depressed, and the undissociated substance is precipitated.

The following example will serve to illustrate how the solubility product of a substance can be determined, and how the change in solubility, due to the addition of a substance containing a common ion, may be calculated. The solubility of silver bromate, at 25°, is 0.0081 mol per liter. If we assume complete ionization, the concentration of the ions, Ag^+ and BrO_3^-, will be identical and equal to 0.0081 mol per liter, or

$$(0.0081)\ (0.0081) = s.$$

The solubility of silver bromate in a solution of silver nitrate, containing 0.1 mol of Ag^+ ions, can be calculated from the equation,

$$(0.0081)^2 = (0.0081 + 0.1 - x)\ (0.0081 - x),$$

where x represents the amount of silver bromate thrown out of solution by the addition of 0.1 mol of Ag^+ ion. Since $(0.0081 - x)$ represents the concentration of BrO_3^- ions, after the addition of the silver nitrate, it also represents the solubility of silver bromate under similar conditions. The effect of adding a solution of a soluble bromate, con-

taining 0.1 mol of BrO_3^- ion, is the same as that produced by 0.1 mol of Ag^+ ion.

Solubility products are simply special cases of equilibrium constants, and they are calculated in the same way. The application to higher valence types may be illustrated with silver chromate, which has a solubility in pure water of 0.00008 mol per liter. Each molecule which dissolves contributes two silver ions and one chromate ion and

$$s = c^2_{Ag^+} \cdot c_{CrO_4^{--}} = (0.00016)^2\,(0.00008) = 2 \times 10^{-12}.$$

A few solubility products are given in the following table.

SOLUBILITY PRODUCTS AT 25°

AgCl	1.1×10^{-10}	$Mg(OH)_2$	2×10^{-11}
AgBr	7.7×10^{-13}	CaC_2O_4	2.6×10^{-9}
AgI	0.9×10^{-16}	$CaCO_3$	9.3×10^{-8}
$CaSO_4$	6.2×10^{-5}	PbS	1×10^{-28}
$SrSO_4$	2.8×10^{-7}	MnS	1.4×10^{-15}
$BaSO_4$	1.1×10^{-10}	Ag_2S	1.6×10^{-49}
$PbSO_4$	1.0×10^{-8}		

Solubility Product in Concentrated Solutions. The calculation of the solubility product is accurate in pure water with very difficultly soluble salts, for under these conditions the solutions are very dilute. It is necessary, of course, to exclude cases where there is any secondary reaction with the water. For moderately soluble salts the solubility product is not always a constant at a given temperature and, furthermore, the addition of a large quantity of salt usually increases the numerical value of the solubility product.

The deviations from the simple theory may be dismissed by stating that in more concentrated solutions the nature of the solvent has been changed — the salt solution certainly differing from pure water in its solvent properties. They may be interpreted rather satisfactorily, however, on the basis of the interionic attraction theory, which has already been discussed. The solubility of thallous chloride in various salt solutions* comprised one of the first investigations to show the influence of an excess of electrolytes on solubility. In pure water thallous chloride dissolves to the extent of about 0.016 mol per liter; when potassium chloride is added, the solubility is decreased, but when potassium nitrate is added, the solubility is increased — one-tenth of a mol per liter, raising the solubility to 0.019 mol per liter. Potassium nitrate contains no ion common with thallous chloride, and it might

* Bray and Winninghoff, J. Am. Chem. Soc., **33**, 1663 (1911).

be expected to have no effect. It will be remembered that in a saturated solution there is a dynamic equilibrium with molecules or ions going into solution from the crystal and returning to the crystal. The rate of escape of ions from the crystal is not influenced by the addition of electrolytes to the solution, but the number of collisions on the crystal from solution is decreased by the addition of ionized substances because each positive ion is drawn inward by a mass of negative ions and each negative ion by a mass of positive ions. The situation is like that described on p. 199 where the interionic attraction leads to a decreased vapor-pressure lowering and decreased osmotic pressure, because the *effective* concentration at the surface is decreased. In the case of solubility, a greater total concentration is required to give an effective concentration sufficient to maintain equilibrium conditions with the crystal. Consequently, the analytically determined concentration, or solubility, is increased. It is fair to imagine that potassium chloride itself exerts (1) an effect of interionic attraction which tends to increase the solubility of thallous chloride, and (2) a common ion effect which tends to decrease the solubility.

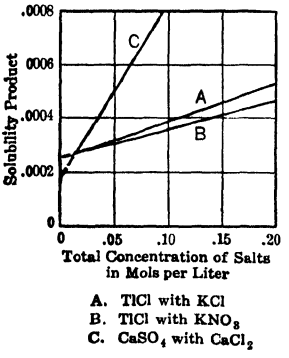


FIG. 128

The increase in solubility due to the addition of any electrolyte leads to a corresponding increase in the solubility product as more electrolyte is added. In Fig. 128 are shown the results with the uni-univalent electrolyte, thallous chloride and the bi-bivalent electrolyte, calcium sulphate. The deviations in the latter case are much greater than the former, as is to be expected on account of the higher ionic strength and the greater interionic attraction of the divalent calcium and sulphate ions. If equation (10) applied rigorously all the lines would be horizontal lines, starting from the intercepts on the y-axis.

Hydrolysis. When a salt formed by a weak acid and a strong base, such as sodium acetate, is dissolved in water, the solution shows an alkaline reaction because some of the hydrogen ions from the water are bound up in the undissociated acetic acid, leaving an excess of hydroxyl ions. The facts are represented by the following equations:

$$\begin{array}{lcl} NaC_2H_3O_2 & \rightleftharpoons & Na^+ + C_2H_3O_2^- \\ & & + \quad + \\ H_2O & \rightleftharpoons & OH^- + H^+ \\ & & \downarrow\uparrow \quad \downarrow\uparrow \\ & & NaOH \quad HC_2H_3O_2 \end{array}$$

The longer arrows indicate the preponderating reactions. Sodium acetate and sodium hydroxide are largely dissociated whereas water and acetic acid are only slightly dissociated. When positive and negative ions are produced from two different sources, there is a chance of changing partners (the process is called metathesis), and if one of the products is undissociated or insoluble, hydrolysis occurs. An alkaline reaction is produced if an excess of hydroxyl ions is left from the water and an acid reaction is produced if an excess of hydrogen ions is left.

Ammonium chloride hydrolyzes in water to give an acid reaction because some of the hydroxyl ions from the water are removed as ammonium hydroxide, leaving an excess of hydrogen ions.

Ferric chloride hydrolyzes to give an acid reaction because the hydroxyl ions are removed in ferric hydroxide, which is very insoluble.

Sodium chloride does not hydrolyze because the only new products which can be formed with water are sodium hydroxide and hydrochloric acid, and these are both completely dissociated.

In general the reaction between a dissolved salt and the water is called hydrolysis, and the general equation may be written

$$BA + H_2O \rightleftarrows BOH + HA, \tag{11}$$

where B is the basic constituent and A the acid constituent of the salt AB.

It is evident then, that hydrolysis (or solvolysis) is due to the removal of either one, or both, of the ions of water by the ions of the salt, to form undissociated, or insoluble substances. As fast as the ions of water are removed, the loss is made good by the dissociation of more water, until eventually, a condition of equilibrium is established. The conditions governing hydrolytic equilibrium may be determined from a knowledge of the solubilities and ionization constants of the substances involved. Thus, if the product of the concentrations of the ions, B^+ and OH^-, exceeds that which can exist in the solvent, then some undissociated, or insoluble substance will be formed. This will disturb the equilibrium of H^+ and OH^- ions, and a further dissociation of water will occur, until the ionic product of water is just reached. Since

$$c_{H+} \times c_{OH^-} = K_w,$$

the concentration of OH^- ions is given by K_w/c_{H+}, where c_{H+} represents the total concentration of H^+ ions. A similar readjustment will take place when an undissociated or insoluble acid and a dissociated base are formed.

We shall now proceed to consider three different types of hydrolytic

dissociation, namely: — (1) the hydrolysis of a salt of a strong base and a weak acid; (2) the hydrolysis of a salt of a weak base and a strong acid; and (3) the hydrolysis of a salt of a weak base and a weak acid.

(1) *Hydrolysis of a Salt of a Strong Base and a Weak Acid.* This type of reaction may be represented by the general equation

$$B^+ + A^- + H_2O \rightleftarrows B^+ + OH^- + HA.$$

The equilibrium constant, K, of this equation is

$$K = \frac{c_{HA} \cdot c_{OH^-}}{c_{H_2O} \cdot c_{A^-}}.$$

The molecular concentration of water is regarded as constant and the hydrolysis constant K_h is

$$K_h = \frac{c_{HA} \cdot c_{OH^-}}{c_{A^-}}. \tag{12}$$

Since $K_w = c_{H^+} \cdot c_{OH^-}$, it follows that

$$c_{OH^-} = \frac{K_w}{c_{H^+}}. \qquad \text{Also} \quad K_a = \frac{c_{H^+} \cdot c_{A^-}}{c_{HA}}.$$

Substituting these values in equation (12), we have

$$K_h = \frac{c_{HA} \cdot K_w}{c_{H^+} \cdot c_{A^-}} = \frac{K_w}{K_a}. \tag{13}$$

If the degree of hydrolysis in a solution containing C gram-equivalents of salt per liter is denoted by x, we may write

$$c_{HA} = xC, \quad c_{OH^-} = \alpha_b x C, \quad \text{and} \quad c_{A^-} = \alpha_s (1 - x)C,$$

where α_b and α_s denote the degrees of dissociation of the base and salt, respectively. On substituting these values in equation (12), we have

$$K_h = \frac{\alpha_b C x^2}{\alpha_s (1 - x)} = \frac{K_w}{K_a}. \tag{14}$$

Assuming that both salt and base are completely dissociated, $\alpha_b = \alpha_s = 1$, and equation (14) becomes

$$K_h = \frac{Cx^2}{(1 - x)} = \frac{K_w}{K_a}. \tag{15}$$

If $(1 - x)$ differs but little from unity, equation (15) may take the form

$$x = \sqrt{\frac{K_w}{K_a C}}. \tag{16}$$

(2) *Hydrolysis of a Salt of a Weak Base and a Strong Acid.* The reaction is represented by the equation

$$B^+ + A^- + H_2O \rightleftarrows H^+ + A^- + BOH. \tag{17}$$

It can be shown in a manner similar to that described under (1), that

$$K_h = \frac{K_w}{K_b} = \frac{Cx^2}{(1-x)}. \tag{18}$$

(3) *Hydrolysis of a Salt of a Weak Base and a Weak Acid.* This type of reaction may be represented by the equation

$$B^+ + A^- + H_2O \rightleftarrows BOH + HA,$$

while the equilibrium constant is given by the equation

$$K = \frac{c_{BOH} \cdot c_{HA}}{c_{H_2O} \cdot c_{B^+} \cdot c_{A^-}}. \tag{19}$$

But $$K_b = \frac{c_{B^+} \cdot c_{OH^-}}{c_{BOH}}, \quad \text{or} \quad c_{BOH} = \frac{c_{B^+} \cdot c_{OH^-}}{K_b},$$

and similarly

$$K_a = \frac{c_{H^+} \cdot c_{A^-}}{c_{HA}}, \quad \text{or} \quad c_{HA} = \frac{c_{H^+} \cdot c_{A^-}}{K_a}.$$

On substituting the foregoing values in equation (19), and assuming as before that the concentration of water is constant, we have

$$K_h = \frac{c_{H^+} \cdot c_{OH^-}}{K_a \cdot K_b} = \frac{K_w}{K_a \cdot K_b}. \tag{20}$$

Since both acid and base are only slightly dissociated, we may write $c_{HA} = c_{BOH} = xC$ and $c_{B^+} = c_{A^-} = \alpha_s(1-x)C$. Assuming that the salt is completely dissociated, $\alpha_s = 1$, and on substituting the preceding values in equation (19), we have

$$K_h = \frac{x^2}{(1-x)^2} = \frac{K_w}{K_a K_b}. \tag{21}$$

On the assumption that the salt is slightly hydrolyzed and $(1-x)$ is nearly equal to 1, equation (21) may be written in the form,

$$x = \sqrt{\frac{K_w}{K_a K_b}}. \tag{22}$$

Salts belonging to the third type give, as a first approximation, a constant degree of hydrolysis regardless of the dilution.

As an illustration of the application of the foregoing equations, we may take the calculation of the degree of hydrolytic dissociation of

potassium cyanide in 0.1 molar solution, at 25°. Potassium cyanide being a salt of a weak acid, the degree of hydrolysis can be calculated by means of equation (15),

$$\frac{Cx^2}{(1-x)} = \frac{K_w}{K_a} = K_h.$$

Since at 25° C., $K_a = 7.2 \times 10^{-10}$ and $K_w = (1.05 \times 10^{-7})^2$, we have

$$K_h = \frac{K_w}{K_a} = \frac{(1.05 \times 10^{-7})^2}{7.2 \times 10^{-10}},$$

and

$$\frac{0.1\,x^2}{(1-x)} = \frac{(1.05 \times 10^{-7})^2}{7.2 \times 10^{-10}},$$

hence

$$x = 0.0123.$$

In addition to the electrical conductance method outlined in the preceding chapter (p. 394), the degree of hydrolysis may also be determined by measuring the catalytic effect of the hydrogen, or hydroxyl ion on the rate of inversion of sugar,* or on the rate of decomposition of diazoacetic ester.†

Another method, of limited applicability, to which we shall refer in the following chapter, involves the calculation of the hydrogen ion concentration in a partially hydrolyzed solution from measurements of electromotive force.‡

The Ionization Constant of Water. One of the most accurate methods for the determination of the ionization constant of water is based upon measurements of the degree of hydrolytic dissociation of different salts. Thus, Shields§ found that an 0.1 molar solution of sodium acetate is 0.008 per cent hydrolyzed at 25°. We may consider the salt, as well as the sodium hydroxide formed from its hydrolysis, to be completely dissociated at this dilution. The ionization constant of the acetic acid formed is 0.000018, at 25°. Solving equation (15) for K_w, we have

$$K_w = K_a \cdot \frac{Cx^2}{(1-x)}.$$

Substituting the above values in this expression, we obtain

$$K_w = 0.000018 \cdot \frac{(0.00008)^2}{(1-0.00008) \times 10} = 1.16 \times 10^{-14},$$

* Ley, Z. physik. Chem., **30**, 222 (1899).
† Bredig and Fraenkel, Z. Elektrochem., **11**, 525 (1905).
‡ Denham, J. Chem. Soc., **93**, 41 (1908).
§ Z. physik. Chem., **12**, 167 (1893).

and since the ions, H^+ and OH^-, are present in equivalent amounts we have

$$c_{H+} = c_{OH^-} = \sqrt{1.16 \times 10^{-14}} = 1.1 \times 10^{-7} \text{ mol per liter.}$$

Kohlrausch obtained from his measurements of the conductance of pure water, at 25°, $c_{H+} = c_{OH^-} = 1.03 \times 10^{-7}$ mol per liter.

The ionization constant of water has been measured by several other independent methods, the agreement between the results being quite satisfactory. The different methods employed may be classified as follows:

(1) Measurement of the conductance of water of a high degree of purity;

(2) Measurement of the hydrolysis of salts;

(3) Measurement of the catalytic effects of H^+ and OH^- on organic reactions;

(4) Measurement of electromotive force (see next chapter).

The following table gives a summary of the various measurements of the ionization constant of water.

IONIZATION OF WATER

$c_{H^+} = c_{OH^-}$ in gram-mols per liter $\times 10^7$

Temp.	I*a*	I*b*	II	III	IV	V*a*	V*b*	VI	Best values*
0°	0.30	0.32	0.37	....	0.34	....	....	....	0.34
18°	0.68	0.73	0.84	....	0.78	....	....	....	0.77
25°	0.90	0.96	1.10	1.1	1.03	1.03	1.07	1.00	1.01
50°	....	....	2.96	....	2.37	2.26	2.37	....	2.35

* Bjerrum, I. C. T., **VI**, 152.

I*a*. Hydrolysis of ammonium diketotetrahydrothiazole; dissociation of salt calculated from conductance measurements. Noyes and Kanolt, Carnegie Inst. Publ., **63**, 346 (1907).

I*b*. A recalculation of I*a*, using activity coefficients (Chapter XVII). Bjerrum, I. C. T. **VI**, 152.

II. Electromotive force of acid-alkali cell; dissociation of electrolytes calculated from conductance measurements. Lorenz and Böhi, Z. physik. Chem., **66**, 733 (1909).

III. Hydrolysis of sodium acetate. Shields. Z. physik. Chem., **12**, 167 (1893).

IV. Conductance of pure water. Kohlrausch and Heydweiller. Ann. Physik., **53**, 209 (1894).

V*a*. Hydrolysis of ammonium borate; dissociation of salt calculated from conductance measurements. Lunden, J. chim. phys., **5**, 574 (1907).

V*b*. A recalculation of V*a*, using activity coefficients. Bjerrum, I. C. T. **VI**, 152.

VI. Mutarotation of glucose by acids and alkalies. Hudson, J. Am. Chem. Soc., **29**, 1571 (1907).

The correctness of these figures can be further checked by taking the values of the degree of ionization of water at two temperatures, and calculating the heat of the reaction,

$$H_2O = H^+ + OH^-,$$

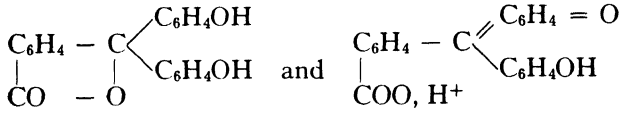
by means of the equation of the reaction isochore. Thus, from the above table, the degree of ionization of water is $(0.34 \times 10^{-7})^2$, at 0°, and $(2.35 \times 10^{-7})^2$, at 50°. Introducing these values into the equation,

$$\Delta H = \frac{2.3026\, R\, (\log K_2 - \log K_1)\, T_2 T_1}{T_2 - T_1}$$

and solving for ΔH we obtain +13,500 calories. This value agrees well with that found for the reverse reaction by the direct measurement of the heat of neutralization of completely ionized acids and bases, viz., −13,800 calories.

Theory of Indicators. When a solution of a base is titrated with an acid, the end-point is reached when the amount of acid added is just equivalent to the amount of base present. Theoretically, the solution at the end of the titration should be identical in composition with a solution prepared by dissolving a known weight of the salt formed in the process of neutralization, in the calculated amount of the solvent. Unless both acid and base have identical ionization constants, however, the salt formed will be hydrolyzed and, therefore, the indicator should change its color when the hydrogen ion concentration of the solution acquires the same value as that which exists in a solution of the salt formed in the process of neutralization.

In order to understand the mechanism of the action of indicators, it must be remembered that indicators are, in almost all cases, weak organic acids which are capable of existing in two tautomeric forms in equilibrium with each other. For example, phenolphthalein has been shown to exist in the two following forms:



One of these forms, which for convenience we may designate by the formula, H*In*, is a non-electrolyte, while the other form, which may be represented by the formula, HIn_1, is an electrolyte and, as such, is ionized in solution. The equilibria existing in a solution of such an indicator-acid may be represented in the following manner:

$$\underset{\text{(color } A\text{)}}{H\mathit{In}} \rightleftarrows H\mathit{In}_1 \rightleftarrows H^+ + \underset{\text{(color } B\text{)}}{\mathit{In}_1^-}$$

The criteria of a good indicator are that there shall be a sharp contrast between the two colors which it exhibits in acid and alkaline media, and that the value of ratio, HIn_1/HIn, shall be small. It is apparent that the addition of a strong acid to a solution containing an indicator-acid will displace the above equilibria toward the left, with the production of the so-called "acid color" of the indicator. In like manner, the addition of a base to the solution of an indicator-acid will displace the equilibria toward the right, with the development of the so-called "alkaline color" of the indicator. The "neutral color" of an indicator is intermediate between the acid and alkaline colors, and is obtained when the concentration of the hydrogen ion in the solution assumes such a value that one-half of the indicator is in the form HIn, and the other half is in the form In_1^- and MIn_1, M being the metal of the added base.

According to the law of mass action,

$$\frac{c_{H+} \times c_{In_1^-}}{c_{HIn}} = K_a, \tag{23}$$

or

$$c_{H+} = K_a \frac{c_{HIn}}{c_{In_1^-}}. \tag{24}$$

If we denote by y the fraction of the indicator which exists in the form exhibiting the alkaline color, then $1 - y$ will represent the portion which is present in the form exhibiting the acid color. Therefore, equation (24) becomes

$$c_{H+} = K_a \frac{(1 - y)}{y}. \tag{25}$$

If the indicator exhibits its neutral color when $y = 0.5$, equation (25) will take the form,

$$c_{H+} = K_a. \tag{26}$$

In other words, when the indicator acquires its neutral color, the indicator constant K_a, is numerically equal to the hydrogen ion concentration of the solution. The value of the fraction y, for different indicators has been determined by measuring the number of cubic centimeters of a solution of a given base which must be added to a solution containing a known amount of indicator to bring about a change of color.* Thus, it has been found that phenolphthalein changes color when $y = 0.1$. The value of the indicator constant K_a,

* Salm, Biochem. Z., **21**, 131 (1909); Prideaux, "Theory of Indicators."

for phenolphthalein, being 1×10^{-10}, it follows that the hydrogen ion concentration, at which the color change occurs, will be

$$c_{H+} = 1 \times 10^{-10} \frac{(1 - 0.1)}{0.1} = 1 \times 10^{-9}.$$

Therefore, phenolphthalein will be a suitable indicator to use in titrations where the hydrogen ion concentration of the solution of the resulting salt is approximately 1×10^{-9}. For example, when acetic acid is titrated with sodium hydroxide, the proper end-point will be reached when the hydrogen ion concentration existing in the solution corresponds to that of a solution of sodium acetate of equivalent concentration. Since sodium acetate is the salt of a weak acid, it follows that its degree of hydrolysis can be calculated by means of equation (15). Substituting the known data in this equation, we have

$$\frac{Cx^2}{(1 - x)} = \frac{1 \times 10^{-14}}{18 \times 10^{-6}},$$

it being assumed that the solution is so dilute that $\alpha_s = \alpha_b = 1$. If the concentration of the sodium acetate at the end-point is 0.1 normal, the degree of hydrolysis will be 7×10^{-5}, and the hydroxyl ion concentration will be 7×10^{-6}. Since $c_{H+} \times c_{OH^-} = 1 \times 10^{-14}$, it follows that the hydrogen ion concentration in the solution will be $1 \times 10^{-14} \div 7 \times 10^{-6} = 1.4 \times 10^{-9}$. That is, the solution is actually slightly alkaline at the end-point, and consequently phenolphthalein, which undergoes a change in color at practically the same hydrogen ion concentration, is a proper indicator to employ in this titration.

REFERENCES

Treatise on Physical Chemistry, Chapter XI. Taylor.
Solutions of Electrolytes. Hammet.
Theory of Indicators. Prideaux.
Indicators. Kolthoff and Furman.

PROBLEMS

1. At 25° the specific conductance of butyric acid at a dilution of 64 liters is 1.812×10^{-4} reciprocal ohms. The equivalent conductance at infinite dilution is 380 reciprocal ohms. What is the degree of ionization and the concentration of H^+ ions in the solution? What is the ionization constant of the acid?

Ans. $\alpha = 0.0305$, $c_{H+} = 4.765 \times 10^{-4}$ gram-ions per liter, $K = 1.5 \times 10^{-5}$.

2. At 18° the specific conductance of a 0.01 *M* solution of formic acid is $4.8 \cdot 10^{-4}$ reciprocal ohms. The equivalent conductance at infinite dilution is 362 at this temperature. What are the values of α, c_{H+} and K?

3. At 40° the ionization constant of ammonium hydroxide is 2×10^{-5}. What is the OH^- ion concentration in a 0.1 *M* solution? What is the OH^- ion concentration

of a solution 0.1 M with respect to ammonium hydroxide which is also 0.1 M with respect to ammonium chloride, assuming the latter to be completely ionized?

4. 1 g. of lactic acid is diluted with water to 500 cc. How many gram-ions of hydrogen ion are present in the solution? The dissociation constant of lactic acid is 1.36×10^{-4}.

5. At 25° the ionization constant of α-bromopropionic acid is 1.06×10^{-3} and that for β-bromopropionic acid is 9.5×10^{-5}. What is the relative strength of these two acids?

6. The ionization constants at 25° for acetic acid, lactic acid and bromoacetic acid are 1.81×10^{-5}, 1.36×10^{-4} and 1.35×10^{-3} respectively. Compare the values of α for a 0.01 M solution of each of these acids as calculated by the approximate method (assuming $1 - \alpha = 1$) and by the exact method.

7. The ionization constant of a 0.05 molar solution of acetic acid is 0.0000175 at 18°, and 0.00001624 at 52°. Calculate the heat of ionization of the acid.

Ans. $\Delta H = -416$ cal.

8. The ionization constant of ammonium hydroxide is 1.4×10^{-5} at 0° C. and 2×10^{-5} at 40° C. What is the average heat of ionization of ammonium hydroxide in this range of temperature?

9. (*a*) The solubility of calcium fluoride is 0.0002 mol per liter at 18°. What is the solubility product?

(*b*) The solubility of lead iodide is 0.7 g. per liter at 18°. What is the solubility product?

Ans. (*a*) 3.2×10^{-11}.

10. At 20° the specific conductance of a saturated solution of silver bromide was 1.576×10^{-6} reciprocal ohms, and that of the water used was 1.519×10^{-6} reciprocal ohms. Assuming that silver bromide is completely ionized, calculate the solubility, and the solubility product of silver bromide, having given that the equivalent conductances of potassium bromide, potassium nitrate, and silver nitrate, at infinite dilution, are 137.4, 131.3, and 121 reciprocal ohms respectively.

Ans. $c_{AgBr} = 4.49 \times 10^{-7}$ mol per liter.

11. At 18° C. the specific conductance of a saturated solution of silver iodate was 1.3×10^{-5} reciprocal ohms. The conductance of the water used was 1.1×10^{-6} reciprocal ohms. Assuming that silver iodate is completely ionized, calculate the solubility and solubility product. The equivalent conductances at infinite dilution of sodium iodate, sodium acetate and silver acetate are 76.94, 78.16, and 88.8 respectively.

12. The solubility of silver cyanate, at 100°, is 0.008 mol per liter. Calculate the solubility in tenth-molar solution of potassium cyanate.

13. The solubility of strontium sulphate at 20° is 0.00055 mol per liter. What is the solubility product? How much strontium sulphate would be dissolved in a solution having a sulphate ion concentration of .05 gram-ions per liter?

14. Calculate the degree of hydrolysis of a 0.1 molar solution of ammonium chloride, having given the following data: $-\alpha_s = 0.86$, $\alpha_a = 0.87$, $K_{NH_4OH} = 0.000023$, and $K_w = (0.91 \times 10^{-7})^2$ at 25°.

Ans. $x = 0.006$ per cent.

15. The hydrolysis constant of potassium cyanide is 8.3×10^{-6} and the ionization constant of hydrocyanic acid is 1.32×10^{-9}. (*a*) To approximately what extent is a 0.01 molar solution of KCN hydrolyzed? (*b*) A 0.001 molar solution?

16. The hydrolysis constant of aniline hydrochloride is 2.25×10^{-5}, and the ionization constant of aniline is 4.2×10^{-10}. Calculate the concentration of the H^+ and OH^- ions in pure water.

17. The hydrolysis constant of potassium cyanide is 8.3×10^{-4} and the ionization

constant of hydrocyanic acid is 1.32×10^{-9}. What is the concentration of H^+ ion in pure water?

18. The value of the indicator constant for methyl orange is $K_a = 5 \times 10^{-4}$ and the indicator changes to its alkaline color when it is nine-tenths neutralized. Show that methyl orange is a suitable indicator to use in the titration of ammonium hydroxide with hydrochloric acid using 0.1 *M* solutions. The ionization constant of ammonium hydroxide may be assumed to be 18×10^{-6}.

19. The value of the indicator constant for rosolic acid is $K_a = 4 \times 10^{-8}$ and the indicator changes to its alkaline color when it is one-tenth neutralized. Would this be a suitable indicator to use in the preceding titration?

20. What is the hydrogen ion concentration at the stoichiometrical point in the titration of 0.2 *M* ammonium hydroxide with 0.2 *M* hydrochloric acid? The ionization constant of ammonium hydroxide is $2 \cdot 10^{-5}$ and the hydrochloric acid and ammonium chloride may be assumed to be completely dissociated. The indicator constants of bromcresol purple, phenol red and phenolphthalein are 5×10^{-7}, 2×10^{-8} and 10^{-10} respectively. If the end-point is determined in each case when the indicator is one-tenth neutralized, i.e., one-tenth in the form exhibiting the alkaline color, show that bromcresol purple is best suited for the above titration.

CHAPTER XVII

ELECTROMOTIVE FORCE

Galvanic Cells. The behavior of solutions and electrodes during the passage of electricity has been studied in an earlier chapter and now our attention will be occupied with the electrical potentials developed when electrodes are introduced into solutions of electrolytes. In the former case chemical changes were produced at the expense of electrical energy; in the present case electrical phenomena are produced by spontaneous chemical changes.

Since the year 1800, when Volta invented his electric pile, many different forms of galvanic cells have been introduced. It is not our purpose to give a detailed account of these cells but rather to discuss their theory and their use in physical chemical measurements. One of the oldest and simplest cells is the Daniell cell, consisting of a zinc electrode immersed in zinc sulphate and a copper electrode immersed in copper sulphate, the two solutions being separated from each other by a porous cup. The electromotive force of such a cell is about 1 volt, the zinc electrode being negative and the copper positive.

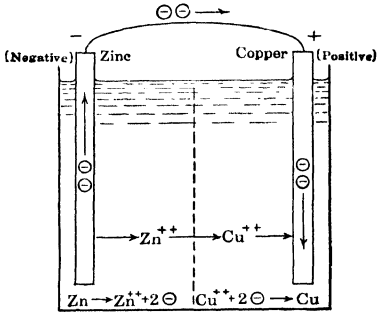


FIG. 129

The operation of the cell may be understood with the help of Fig. 129. On one electrode there is a tendency for zinc atoms to lose their two valence electrons and produce zinc ions which dissolve in the solution; at the other electrode there is a tendency for the copper ions to take two electrons from the electrode. If the electrodes are not connected, these reactions will proceed only to an infinitesimal extent because charges are built up on the electrodes which prevent further action. When the electrodes are connected with a wire, the electrons from the zinc electrode move to the copper electrode (repelled by the negative and attracted by the positive electrode), the charges on the electrodes are removed, and so the reactions go on. Faraday's law applies, and for each gram-equivalent of zinc which ionizes, 96,500 coulombs of electricity, or 6.06×10^{23} electrons, travel around the wire to the copper

electrode and deposit 1 gram-equivalent of copper atoms from among the many copper ions which collide with the electrode. This transfer of electrons along the wire can be made to do useful work, the amount of which depends not only on the number of electrons (the capacity factor) but also on the difference in potential (the intensity factor).

As long as only a moderate current is drawn from the cell the original nature of the electrodes is not modified, the only change being the gradual depletion of the copper ions due to the separation of copper and their replacement by zinc ions. If the circuit is left open, the copper ions will diffuse and deposit on the zinc electrode. In this way, miniature local galvanic cells will be formed on the surface of the zinc, and the zinc will ionize continuously as though the main circuit were closed. The porous cup, as represented by the dotted line in Fig. 129, decreases the diffusion. Unless chemically pure zinc is used, local action is likely to occur, owing to the formation of local galvanic couples between the impurities in the electrode and the zinc. This action may be prevented by amalgamating the zinc electrode. In this process the mercury coats over the impurities. The saturated amalgam has the same potential as the pure electrode unless a chemical compound is formed.

The Measurement of Electromotive Force. A simple voltmeter cannot be used for measuring the electromotive force of a small cell because the operation of the voltmeter draws some current which polarizes the electrodes, owing to the deposition of the products of electrolysis. Furthermore, if any appreciable current is drawn, the internal resistance of the cell is a complicating factor, for, according to Ohm's law, $E = I(R + r)$, where R is the resistance of the external circuit and r is the internal resistance of the cell. The fall of potential IR in the external circuit will be equal to E only when r is negligible in comparison with R.

To avoid these difficulties, the electromotive force is usually measured by a compensation method in such a way that practically no current flows through the cell. A voltmeter may be used in connection with a galvanometer as shown later on p. 465, but for accurate measurements a potentiometer is used.

In the Poggendorf compensation method, the electromotive force to be measured is just balanced by an equal and opposite electromotive force, so that no current passes. The arrangement of the apparatus for such measurements is shown in Fig. 130. If the two ends of the resistance wire, AB, of uniform cross section, are connected to a lead storage battery C, there will be a uniform fall of potential along its entire length. The amount of fall along any portion AD will be pro-

portional to the length AD, and equal to the fraction AD/AB of the total fall of potential along the entire length of the wire. Now let one terminal of a cell, whose electromotive force is less than that of C, be connected to A, and the other terminal be connected, through a

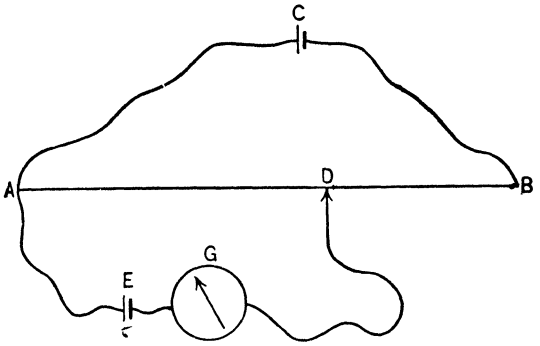


FIG. 130

galvanometer G, with a sliding contact D, the two cells, E and C, working in opposition.

As the contact D is moved along the wire, the galvanometer will deflect in one direction when the potential drop between A and D is greater than the voltage of the cell E, and in the opposite direction when it is less. When the two are exactly equal, the galvanometer will register zero, and then

$$\text{e.m.f. of } C : \text{e.m.f. of } E :: AB : AD,$$

from which the value of the electromotive force of the cell E can be calculated. Since the electromotive force of a storage cell is not quite constant, it is customary, after having determined the point D, to substitute a standard cell for E, and balance this against the storage cell, finding a new point of balance, D'. We now have the proportion,

$$\text{e.m.f. of } C : \text{e.m.f. of standard} :: AB : AD'.$$

Combining these two proportions, we obtain

$$\text{e.m.f. of } E : \text{e.m.f. of standard} :: AD : AD'. \qquad (1)$$

The potentiometer makes use of these general principles but introduces an adjustable resistance in such a way that the instrument indicates the voltage directly without involving any calculations. A simplified circuit is shown in Fig. 131. The current from the cell C passes around the circuit which is indicated with heavy lines. It can be varied with the adjustable resistance D by turning a dial or a series

of dials. The circuit includes a series of resistance coils R arranged in a circle, each one having exactly the same resistance. The circuit includes also a circular wire, W, equal in resistance to one of the re-

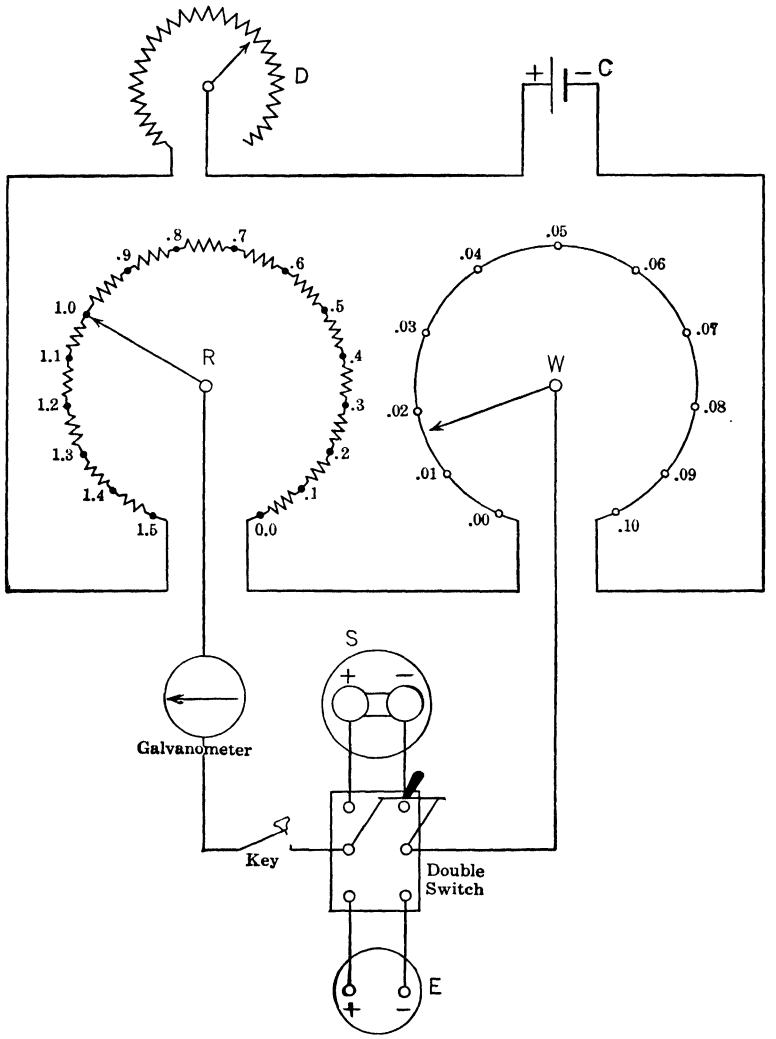


FIG. 131

sistances of R, and divided into 1000 equal parts. By moving the contacts in R and W, it is possible to interpose any part of this resistance and balance the corresponding fall of potential against either the standard cell or the unknown voltage E by means of the galvanometer.

In making a determination of voltage, the double-pole switch is thrown to include the standard cell S, and the contacts in R and W are set to correspond to the voltage of the particular standard cell used; 1.0183 as shown for example in Fig. 131. The resistance D is then adjusted until the galvanometer shows no deflection when the key is closed. The potential drop across the resistance of 1.0183 units is then 1.0183 volts, and under these conditions the potential drop in volts across any resistance in the circuit is identical with the resistance reading because the same current is flowing at all points in the circuit. Without changing the resistance D the switch is thrown in the opposite direction to include the unknown electromotive force E, and the contacts R and W are adjusted to give a zero reading on the galvanometer. The readings of R and W then give the voltage E directly.

Referring back to equation (1), AD in Fig. 130 is equivalent, in Fig. 131, to the reading of R and W with the cell E; and AD' is equivalent to the reading with the standard cell S. It is evident that by experimental means AD' has been made to have the same value as the electromotive force of the standard cell; and therefore, e.m.f. of $E = AD$. In other words, the electromotive force of any unknown cell is directly equal to the reading obtained on R and W, when the potentiometer has been adjusted with the standard cell.

Standard Cells. It is apparent that the accuracy of all measurements of electromotive force is dependent upon the cell employed as a standard. Much time has been devoted to the study of various reversible cells, with a view to establishing a standard of electromotive force.

The most widely used standard of electromotive force is the so-called Weston or cadmium cell, made up according to the scheme,

Cd, Solution $CdSO_4$, Solution Hg_2SO_4, Hg.

A short platinum wire is sealed through the bottom of each limb of an H-shaped vessel. In one limb is placed a small amount of a 10 to 13 per cent cadmium amalgam, together with a layer of small crystals of $CdSO_4 \cdot \frac{8}{3} H_2O$. In the other limb is placed a small amount of pure mercury, over which is a layer of a paste, composed of solid mercurous sulphate and a saturated solution of cadmium sulphate. The cell is then filled with crystals of cadmium sulphate and a saturated solution of cadmium sulphate, after which the two limbs of the cell are hermetically sealed. If carefully prepared with specially purified materials* this cell will remain unaltered for years and will have an electromotive force, at 20°, of 1.0183 volts. In addition to the fact that it can be so

* Bur. Standards, Bull. **3**, 623 (1907); **4**, 1 (1907).

easily reproduced, the temperature coefficient of the cell is almost negligible.

The electromotive force of a Weston standard cell at any temperature t, is given by the formula,

$$\text{e.m.f. at } t^\circ = 1.0183 - 0.0000406\ (t - 20). \qquad (2)$$

This cell is reversible and, unless abnormally large currents are used, the voltage remains constant. When it operates spontaneously cadmium goes into solution as cadmium ions and the electrons left by this ionization pass around the wire to the positive electrode, where mercurous ions take them up and deposit as mercury atoms. When the cell is opposed by a larger electromotive force, the current flows in the opposite direction, cadmium is deposited and mercury is dissolved. The solution is saturated with respect to both salts, and a fixed concentration is maintained in spite of additions from the electrode or deposition on the electrode. This condition of saturation is maintained no matter which way the current is flowing. The cadmium amalgam is solid and its potential is independent of concentration between 10 and 13 per cent cadmium.

Reference Electrodes. The method commonly employed for the measurement of the difference of potential between a metal and a solution is based upon the use of an electrode in which the difference of potential between the electrode and a certain solution of one of its salts is assumed. Such an electrode is called a *reference electrode*. If a cell is made up by combining the reference electrode with the electrode whose potential is to be determined, it is possible, from measurements of the resulting electromotive force, to calculate the value of the unknown difference of potential. One of the most convenient electrodes to prepare is the normal calomel electrode, a satisfactory form of which is shown in Fig. 132. The bottom of the electrode vessel is covered with a layer of pure mercury, upon which is poured a paste, prepared by rubbing together in a mortar mercury and calomel, moistened with a molar solution of potassium chloride. The vessel is then filled with a molar solution of the same salt which has been saturated with calomel by prolonged shaking with the latter. Connection with the mercury is established by means of a platinum wire sealed into a glass tube A, the latter being passed through the rubber stopper which closes the vessel. In using the calomel electrode, the bent side tube, C, is filled with molar potassium chloride by applying suction at the side tube B, which is then closed by means of a pinch-cock.

Attempts have been made with a dropping mercury electrode and with supposedly "null" electrodes to establish the absolute potential

of a reference electrode, but they are now regarded as unsatisfactory.*

Since the absolute potentials of single electrodes are unknown, it becomes necessary to assign an arbitrary value to some one electrode as a starting-point. Sometimes the normal calomel electrode is assigned a value of zero, but the normal hydrogen electrode has come to be quite generally accepted as the standard, and it will be used throughout this book. The normal hydrogen electrode with an assigned voltage of zero consists of a strip of platinized platinum partly immersed in a solution of hydrochloric acid which is normal with respect to hydrogen ions, i.e., a solution whose *effective* concentration is 1 gram-ion of hydrogen ions per 1000 g. of water.† The electrode is bathed with hydrogen gas at 1 atmosphere pressure. This electrode is more troublesome to use than the calomel electrode, and so it is customary to make the actual measurements with the normal calomel electrode, taking its potential as +0.281 volt; it has been found by careful experimental measurements that the normal calomel electrode is 0.281 volt more positive than the normal hydrogen electrode.

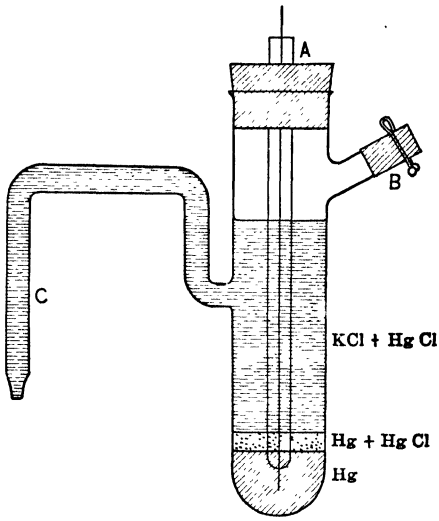


FIG. 132

The normal calomel cell, the tenth-normal and the saturated calomel cells are used, the terms referring to the concentration of the potassium chloride. The potential of the normal calomel electrode at 25° is +0.281, of the tenth-normal is +0.336, and of the saturated is +0.246 volt with reference to the normal hydrogen electrode.

The potential of any half-cell is easily determined in terms of the arbitrary zero of potential by combining this half-cell with a calomel electrode and measuring the voltage of the whole cell with a potentiometer. The solutions in the two half-cells are connected with a "salt bridge" of potassium chloride. An inverted U-tube filled with solution may be used for the bridge; or side arms, as shown, in Fig.

* They led to a value of +0.56 volt for the normal calomel cell and this value was used in the older literature.

† More exactly the solution of hydrochloric acid surrounding the electrode has an activity of unity.

132, may be dipped into an intermediate connecting vessel containing a solution of potassium chloride. Ammonium nitrate may be used in place of potassium chloride if a precipitate is formed by the chloride.

Reversible Cells. Galvanic cells are either reversible or irreversible. Disregarding the slow process of diffusion, the Daniell cell may be taken as an example of a reversible cell. If an electromotive force slightly less than that of the cell is opposed to that of the cell, the current will still flow in the direction indicated in Fig. 129; but if the external electromotive force exceeds that of the cell, the current will flow in the opposite direction, and zinc will deposit and copper will dissolve. If an appreciable current is drawn from the cell, some of the electrical energy will be wasted as heat and the maximum work cannot be obtained. When only an infinitesimal current is consumed, the system is always practically in a state of equilibrium, and under these conditions the work obtained is the maximum work. This maximum work is definite and it is of great value in thermodynamical calculations, whereas the measurements of irreversible cells are of much less importance.

The maximum work done in the operation of a reversible galvanic cell is obtained very simply by measuring the voltage with a potentiometer and sensitive galvanometer in such a way that the only current consumed is that required to give a slight deflection of the galvanometer (perhaps one-millionth of an ampere) in obtaining the zero point. (This voltage, which is the intensity factor, is then multiplied by the capacity factor, 96,500 coulombs, to obtain the maximum work in joules per gram-equivalent of material.)

Electrodes involving the formation of certain oxides are examples of irreversible electrodes. Sometimes it is possible to determine from the experimental behavior of a cell that it is irreversible as, for example, when mechanical agitation produces marked unsteadiness in voltage, or when the cell does not return to the same voltage after allowing a larger current to pass momentarily.

Relation between Chemical Energy and Electrical Energy. When a cell operates reversibly at constant pressure, the electrical work obtained per gram-atom is nFE, where n is the valence, F is the faraday or 96,500 coulombs, and E is the voltage. This maximum work in joules may be converted into calories by dividing by 4.185. Then F corresponds to 23,060 calories per volt. In addition to the electrical work, some pressure-volume work may be done also, as, for example, when a gas is evolved against the atmospheric pressure. Since the work is done reversibly, it is independent of the path, and the total work done, including both electrical and pressure-volume work, is also

a measure of the decrease in work content, $-\underline{\underline{\Delta A}}$. The pressure-volume work may be excluded from consideration by using the decrease in free energy, $-\Delta F$, instead of $-\underline{\underline{\Delta A}}$, because at constant pressure (p. 132)

$$-\underline{\Delta F} = -\underline{\underline{\Delta A}} - \underline{\underline{p\,\Delta v}}. \tag{3}$$

Then under all conditions of constant pressure, whether or not there is a volume change, the decrease in free energy is equal to the electrical work done, and

$$-\Delta F = nFE. \tag{4}$$

The relation between chemical energy and heat energy has been discussed in the chapter on thermodynamics (p. 133) where the Gibbs-Helmholtz equation was derived, giving the following equation:

$$\Delta F - \Delta H = T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p \tag{5}$$

Substituting for ΔF its equivalent, $-nFE$,

$$nFE = -\Delta H + nFT\frac{\partial E}{\partial T} \tag{6}$$

$$E = \frac{-\Delta H}{nF} + T\frac{\partial E}{\partial T}. \tag{7}$$

This equation expresses the electromotive force of a reversible cell in terms of the temperature coefficient of the cell, and the heat of the chemical reaction occurring within the cell. It may be used to calculate the heat of reaction from the measured voltage and the temperature coefficient of voltage. Since the precision of electrical measurements is in general greater than that of thermal measurements, this indirect method often gives results which are more accurate than the calorimetrically determined values. Applying this equation to the Cd-Ag cell at 25° C. where the voltage is 0.67531, and the temperature coefficient is -0.00065 volt per degree,

$$-\Delta H = \frac{nF}{4.185}\left(E - T\frac{\partial E}{\partial T}\right) = \frac{2 \times 96{,}500}{4.185}(0.67531 + 298 \times 0.00065)$$
$$= 40{,}076 \text{ cal.} \tag{8}$$

The heat of reaction as determined in a calorimeter is 39,530.

Further examples are given in the following table. It will be seen that the agreement between the calculated and the experimental values of ΔH is entirely satisfactory.

A comparison of the last two columns is particularly interesting. The electrical energy in calories, $nFE/4.185$, given in the last column,

is also the decrease in free energy and a measure of chemical affinity. Sometimes the maximum work done is greater than the heat evolved and sometimes it is less. It is evident from equation (6) that if the temperature coefficient is positive, the work, $nFE/4.185$, which can be done by the cell will be greater than the heat which is evolved in the reaction, and that if the temperature coefficient is negative, the work will be less than the heat evolved.

EXPERIMENTAL VERIFICATION OF GIBBS–HELMHOLTZ EQUATION

Cell	E	$\partial E/\partial T$	$-\Delta H$ equation (7)	$-\Delta H$ (obs.) calorimeter	$\frac{nFE}{4.185}$
Zn, $ZnCl_2(0.555m)$, AgCl, Ag.(0°)	1.015	−0.000402	51,989	52,046	46,810
Cd, $CdCl_2 \cdot 2\frac{1}{2}\ H_2O$(sat), AgCl, Ag.(25°)	0.67531	−0.00065	40,076	39,530	31,140
Cd, $CdCl_2 \cdot 2\frac{1}{2}\ H_2O$ (sat), $PbCl_2$, Pb.(25°)	0.18801	−0.00048	15,250	14,650	8,670
Pb, $Pb(C_2H_3O_2)_2$ $(0.555m)\|Cu(C_2H_3O_2)_2$ (sat), Cu.(0°)	0.4764	+0.000385	16,900	17,533	21,980

In the special case where the voltage of the cell is independent of temperature ($\partial E/\partial T = 0$), the heat of reaction and the work are the same.

Some of the first cells to be studied, including the zinc-copper cell, had such a small temperature coefficient that it was falsely assumed for a while that the heat evolved is a measure of the chemical affinity. Occasionally, even yet, when adequate data are not available the heat of reaction is taken as an approximate indication of the chemical affinity, but such estimates are subject to great uncertainties and may lead to erroneous conclusions.

It may seem a little surprising, at first, that it is possible to obtain more work from a cell than corresponds to the heat of reaction. When lead displaces a gram-atom of copper from copper acetate for example, 17,533 calories of heat is evolved, but when a battery is composed of copper and lead electrodes in solutions of the acetates it is theoretically possible to obtain 21,980 calories of work per gram-atom from the same reaction. Such a cell tends to cool off when it operates and it thus absorbs heat from the surroundings which is then converted into more work. On the other hand if the maximum electrical work of a

cell is less than the heat of the reaction, some of the energy is dissipated as heat, i.e., the cell tends to heat up while it operates.

Conventions Regarding Signs. Much useful information may be obtained from the signs given to cell potentials and electrode potentials. The following conventions will be followed.

(1) The negative electrode in a galvanic cell, i.e., the one connected to the negative terminal of a voltmeter or potentiometer, may be considered to have the higher "electron pressure." *Outside* the cell electrons flow from the negative electrode to the positive when the cell is operating spontaneously. *Inside the cell the negative electricity moves toward the negative electrode*, creating thereby a greater electron pressure.

(2) The voltage of a galvanic cell may be either positive or negative, depending on the order in which parts of the cell are written and on arbitrary conventions. *If negative electricity flows inside the cell from right to left* (i.e., electrons are taken from the right electrode and left at the left electrode), *the voltage is said to be positive.*

If the voltage E, of the cell as written, is positive, the work done, corresponding to the chemical reaction of the cell, is positive and the free energy of the cell is *decreased* in accordance with the equation

$$nFE = w = -\Delta F. \tag{9}$$

Under these conditions the cell operates spontaneously, for it will be remembered that spontaneous reactions are possible only when the free energy decreases (p. 132).

These conventions are in common use by American investigators, and they are in agreement with Lewis and Randall's "Thermodynamics and the Free Energy of Chemical Substances," with Taylor's "Treatise on Physical Chemistry," and with the International Critical Tables.

(3) *The voltage E of a galvanic cell is regarded as the algebraic sum of the potential E_1 of the first electrode and the potential E_2 of the second electrode*, care being taken to make the order in which the electrolyte and electrode are written the same as that in which they occur in the actual cell.

$$E = E_1 + E_2 = E_l + E_r.^* \tag{10}$$

(4) *The potential of a single electrode or half-cell is determined by reference to the normal hydrogen electrode. The normal hydrogen electrode is placed at the left* for reference and combined with the

* In this equation the two electrode potentials are written in opposite order (electrode, electrolyte) + (electrolyte, electrode), as they occur in the cell. In case they are both written (electrode, electrolyte), the equation becomes $E = E_1 - E_2$.

electrode in question at the right. The voltage of the resulting galvanic cell is a direct measure of the single electrode potential, because the single electrode potential of the normal hydrogen electrode is taken as zero. The sign of the single electrode potential is determined by the convention given above, that the voltage is positive if negative electricity moves from right to left in the cell as written, when the cell is operating spontaneously. Since the hydrogen electrode is at the left, the other electrode is written in the order *electrolyte, electrode,* and a positive value for the single electrode means that negative electricity flows from the electrode to the solution surrounding the electrode — i.e., the electrode becomes positive with respect to the solution. In the same way a negative single electrode potential signifies that when connected to a hydrogen electrode the negative electricity flows from the solution to the electrode — i.e., the electrode becomes negative with respect to the solution. The sign of an electrode gives the sign of the charge of the *electrode* against the solution, when connected to a normal hydrogen electrode.

These conventions give to the normal sodium electrode (written Na^+, Na) a negative sign and to the normal chlorine electrode (written Cl^-, Cl_2) a positive sign. The sign of the single electrode potentials is then in accord with practical, laboratory connections and in agreement with earlier editions of this book.

(5) In order to show the relation between the way a cell is written and the chemical reaction which takes place in the cell, a fifth convention is necessary.

The chemical reaction of a cell is written as that reaction which would cause negative electricity to flow from right to left within the cell. This "cell reaction" may be spontaneous as in discharging a cell, or non-spontaneous as in charging. It may be written by adding together that reaction in the left half-cell which makes the electrode negative, and that reaction in the right half-cell which makes the electrode positive.*

The signs in electrochemistry are quite confusing because conflicting conventions are used. In the early development of the subject attention was centered on positive electricity, and the direction of movement of positive electricity was called the direction of the current. It now seems best to center our attention on the electron, which is the unit of negative electricity. Accordingly the current will be thought of in terms of an electron stream, and electrons leave the negative electrode and pass along a wire to the positive electrode. An arrow above the cell indicates the direction of the electron stream outside

* In other words when the voltage is positive, the reduced form at the left and the oxidized form at the right react spontaneously (p. 436).

the cell. Through the cell the current is carried by both negative and positive ions, but at the surface of the electrodes the transfer of electricity is effected only by electrons and again the arrows *below* the cell indicate the direction of the electron movement across phase boundaries *in* the cell.

It must be strongly emphasized that this convention is contrary to that used in many books (including earlier editions of this book) where the arrows refer to the direction of positive electricity. An *e* will be attached to these arrows as a reminder that they refer to the movement of *electrons* rather than positive current.

The various conventions which have been described are illustrated by the following cells and half-cells.

$$\underset{\leftarrow e}{\overset{e\longrightarrow}{\mathrm{Zn},\ Zn^{++}\ (a=1)\ \|\ H^{+}\ (a=1),\ H_2\ (1\ \text{atmos.})^{*}}} \qquad E = +0.7618$$

$$E = E_1 + E_2. \qquad E_2 = 0. \quad \text{Therefore } E_1 = E_{Zn,\,Zn^{++}} = +0.7618.$$

In order for negative electricity to flow from right to left within the cell, Zn must go into solution as Zn^{++} at the left electrode and H^+ must be converted into H_2 at the right electrode. The reactants are thus Zn and H^+ and the products Zn^{++} and H_2, the reaction being written

$$Zn + 2\,H^{+} \rightarrow Zn^{++} + H_2 \qquad E = 0.7618.$$

$$\Delta F = -nFE = \frac{-2 \times 96{,}500 \times 0.7618}{4.185} = -35{,}000 \text{ cal.}$$

By experiment the potential of the cell is found to be 0.7618 volt with the zinc electrode negative. Since negative electricity moves inside the cell from right to left, the voltage of the cell is arbitrarily taken as positive. A positive voltage means that the work, nFE, is positive, that the cell does work on its surroundings and uses up its free energy, i.e., ΔF has a negative value. In other words, the reaction is spontaneous; zinc is converted into zinc ions, and hydrogen ions are converted into hydrogen. This cell may be written in the reverse order, thus

$$\underset{e\longrightarrow}{\overset{\leftarrow e}{H_2\ (1\ \text{atmos.}),\ H^{+}\ (a=1)\ \|\ Zn^{++}\ (a=1),\ Zn.}} \qquad E = -0.7618$$

$$E = E_1 + E_2 \qquad E_1 = 0. \quad E_2 = E_{Zn^{++},\,Zn} = -0.7618.$$

Since negative electricity flows from left to right inside the cell, the potential is defined as negative. Then (nFE) is negative and ΔF is positive, and the cell does not operate spontaneously in the direction

* a = activity or effective concentration (pp. 274, 448). $\|$ indicates the elimination of the junction potential between solutions (p. 448).

indicated. In other words, hydrogen at atmospheric pressure does not react with zinc ions to produce metallic zinc.

The electrode potential of zinc, $E_{Zn^{++},Zn}$ is -0.7618 because the potential of the whole cell is -0.7618 and the potential of the hydrogen electrode is taken as zero. The cell is arbitrarily arranged with the hydrogen electrode on the left so that the zinc ions come at the left of the zinc electrode.

Taking next an electrode which is more positive than the hydrogen electrode,

$$\overset{e\longrightarrow}{\mathrm{H_2\ (1\ atmos.),\ H^+}\ (a=1)\ \|\ \mathrm{Cu^{++}}\ (a=1),\ \mathrm{Cu}}\quad E=+0.3441.$$

$$E_1=0. \qquad E_2=E_{Cu^{++},Cu}=+0.3441.$$

$$\mathrm{H_2+Cu^{++}\rightarrow Cu+2\,H^+}\quad E=0.3441.$$

E being positive, ΔF is negative and the reaction takes place as written, i.e., hydrogen (at one atmosphere) reacts with copper ions at unit activity to produce metallic copper and hydrogen ions at $a=1$.

The potential of the lead electrode is determined from the following cell,

$$\overset{\longleftarrow e}{\mathrm{H_2,\ H^+}\ (a=1)\ \|\ \mathrm{Pb^{++}}\ (a=1),\ \mathrm{Pb}}\quad E=-0.122.\quad E_{Pb^{++},Pb}=-0.122.$$

With cells of these types it has been possible to build up the table of normal electrode potentials given on p. 442.

These normal electrode potentials may then be combined to give the voltage of galvanic cells as illustrated below

$$\mathrm{Zn,\ Zn^{++}}\ (a=1)\ \|\ \mathrm{Cu^{++}}\ (a=1),\ \mathrm{Cu}$$

$$E=E_1+E_2=E_{Zn,Zn^{++}}+E_{Cu^{++},Cu}=0.7618+0.3441=1.1059.$$

Since the voltage is positive for the cell as written, negative electricity flows inside the cell from right to left and the zinc electrode will be the negative electrode. Since the voltage is positive, ΔF is negative and the reaction

$$\mathrm{Zn+Cu^{++}\rightarrow Zn^{++}+Cu}$$

is spontaneous, i.e., zinc displaces copper from solution.

Writing the cell in the reverse order,

$$\mathrm{Cu,\ Cu^{++}}\ (a=1)\ \|\ \mathrm{Zn^{++}}\ (a=1),\ \mathrm{Zn}$$

$$E=E_{Cu,Cu^{++}}+E_{Zn^{++},Zn}=-0.3441+(-0.7618)=-1.1059.$$

Negative electricity flows from left to right inside the cell and the reaction as written, according to the convention, is not spontaneous. To make copper go into solution as copper ions and zinc ions deposit out as zinc atoms, it is necessary to apply external work, i.e., to apply a potential to the cell greater than 1.1059 volts.

In case both electrodes are above hydrogen in the series, the conventions may still be applied. For example,

$$\mathrm{Zn},\ \mathrm{Zn^{++}}\ (a = 1)\ ||\ \mathrm{Pb^{++}}\ (a = 1),\ \mathrm{Pb}$$

$$E = E_{\mathrm{Zn},\,\mathrm{Zn^{++}}} + E_{\mathrm{Pb^{++}},\,\mathrm{Pb}} = +0.7618 + (-0.122) = 0.6398.$$

$$\mathrm{Zn} + \mathrm{Pb^{++}} \rightarrow \mathrm{Zn^{++}} + \mathrm{Pb} \quad E = 0.6398.$$

Since the voltage of the galvanic cell is positive, the reaction as written is spontaneous and zinc therefore must replace lead from solution.

These conventions are applicable also to negative ions as shown with the chloride ion, chlorine cell.

$$\mathrm{H_2},\ \mathrm{H^+}\ (a = 1)\ ||\ \mathrm{Cl^-}\ (a = 1),\ \mathrm{Cl_2}. \quad E = +1.358. \quad E_{\mathrm{Cl^-},\,\mathrm{Cl_2}} = +1.358.$$

(e flows from left to right)

(e flows from right to left)

The reactions at the electrodes which would cause negative electricity to flow from right to left within the cell are $\mathrm{H_2} \rightarrow 2\ \mathrm{H^+}$ and $\mathrm{Cl_2} \rightarrow 2\ \mathrm{Cl^-}$ and the cell reaction is

$$\mathrm{H_2} + \mathrm{Cl_2} \rightarrow 2\ \mathrm{H^+} + 2\ \mathrm{Cl^-}$$

Since the hydrogen electrode at the left is the negative electrode, electrons flow from right to left in the cell (i.e., they leave the chlorine electrode and go into solution attached to chlorine atoms giving chloride ions) and the electrode potential of chlorine ($E_{\mathrm{Cl^-},\,\mathrm{Cl_2}}$) is positive.

Chemical Equilibria and Electromotive Force. It was shown on p. 429 that

$$-\Delta F = nFE \tag{11}$$

and it was shown on p. 272 that in a reaction

$$aA + bB = gG + hH$$

$$-\Delta F = RT \ln K - RT \ln \frac{a^g_G \cdot a^h_H}{a^a_A \cdot a^b_B}. \tag{12}$$

When the reacting materials and products are all at unit activity (i.e., the "effective" concentration is 1 mol per 1000 grams of solvent), ΔF is written ΔF^0 and the last term becomes zero. Thus

$$-\Delta F^0 = RT \ln K. \tag{13}$$

Substituting equation (11) into equation (12)

$$E = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln \frac{a^g_G \cdot a^h_H}{a^a_A \cdot a^b_B}. \tag{14}$$

Also, in the special case where the reactants and products are all at unit activity equation (14) becomes

$$E^0 = \frac{RT}{nF} \ln K. \tag{15}$$

Substituting equation (15) into equation (14)

$$E = E^0 - \frac{RT}{nF} \ln \frac{a^g_G \cdot a^h_H}{a^a_A \cdot a^b_B}. \tag{16}$$

Applying equation (15) to the cell,

$$\text{Zn, } Zn^{++} (a = 1) \parallel Cu^{++} (a = 1), \text{ Cu} \qquad E^0 = 1.1059.$$

Where the reaction is

$$Zn + Cu^{++} = Cu + Zn^{++}$$

$$1.1059 = \frac{RT}{nF} \ln K = 0.029 \log K \tag{17}$$

we have

$$K = \frac{a_{Zn^{++}}}{a_{Cu^{++}}} = 10^{38}. \tag{18}$$

In other words, when zinc is added to a solution of copper, a state of equilibrium is reached in which the effective concentration of the zinc ions is 10^{38} as great as that of the copper ions, that is to say, there are practically no copper ions left in solution.

In the cell Sn, $Sn^{++} \parallel Pb^{++}$, Pb, which has a voltage of only 0.014, K has a value of 4.83, and at equilibrium the effective concentration of Sn^{++} ions is only 4.83 times as great as that of the Pb^{++}.

Oxidation and Reduction Potentials. Oxidation is the *process in which a substance loses electrons, and reduction is the process in which a substance takes on electrons*. Thus, every electrochemical change involves oxidation and reduction. Oxidation occurs at the anode and reduction at the cathode when a current of electricity is passed through the cell. For example, ferrous iron is oxidized at the anode,

$$Fe^{++} \rightarrow Fe^{+++} + e,$$

and ferric iron is reduced to ferrous iron at the cathode,

$$Fe^{+++} + e \rightarrow Fe^{++}.$$

The following reactions illustrate further the reduction process:

$$Zn^{++} + 2e \rightarrow Zn$$
$$Cl_2 + 2e \rightarrow 2Cl^-$$
$$Fe(CN)_6^{---} + e \rightarrow Fe(CN)_6^{----}.$$

The following reactions illustrate the oxidation process:

$$Zn \rightarrow Zn^{++} + 2e$$
$$2Cl^- \rightarrow Cl_2 + 2e$$
$$Fe(CN)_6^{----} \rightarrow Fe(CN)_6^{---} + e.$$

The mutual oxidation and reduction of different ions may be illustrated with the reduction of ferric chloride to ferrous chloride by stannous chloride.

$$2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++}. \tag{19}$$

Electrons move from stannous ions to ferric ions, and the magnitude of this tendency can be determined from the voltage of the corresponding reversible cell, using inert electrodes such as platinum,

$$Pt(Sn^{++}, Sn^{++++}) \,||\, (Fe^{+++}, Fe^{++})\ Pt. \tag{20}$$

The corresponding equation is

$$E = E^0 - \frac{RT}{nF} \ln \frac{a^2_{Fe^{++}} \cdot a_{Sn^{++++}}}{a^2_{Fe^{+++}} \cdot a_{Sn^{++}}}. \tag{21}$$

Reducing ions tend to make an inert electrode more negative, and oxidizing ions tend to make it more positive. When ferrous ions collide with a platinum wire, for example, they tend to give up electrons to the electrode and make it negative, while the ferrous ions themselves tend to become oxidized to ferric ions. Ferric ions, on the other hand, tend to take electrons from the electrode to form ferrous ions and leave the electrode positively charged. The ratio of ferric to ferrous ions around an inert electrode determines its voltage.

As in the case of electrode potentials of metals and their ions it is necessary to refer the reduction-oxidation potentials to some standard, and here again the normal hydrogen electrode is taken as the standard. More often the normal calomel electrode is used for practical convenience, and it is then necessary to add + 0.281 volt to the values thus obtained. The normal oxidation-reduction potentials E^0 are calculated from equation (16). For example, the potential of the ferric-ferrous electrode is obtained from the cell

$$H_2,\ H^+\ (a = 1) \,||\, (Fe^{+++}, Fe^{++})\ Pt. \tag{22}$$

Since the reaction must be written so that negative electricity is transferred from right to left within the cell, the reactant at the right electrode is Fe^{+++}, for in producing Fe^{++} it acquires an electron from the platinum electrode and the result is a transfer of electrons from right to left. By the same convention H_2 is the reactant at the left electrode because the change from hydrogen to hydrogen ions involves the transfer of electrons to the electrode, and within the cell as written, the electrons move to the electrode at the left. The reaction of the whole cell is

$$\tfrac{1}{2}\,H_2 + Fe^{+++} \rightleftarrows Fe^{++} + H^+. \tag{23}$$

Applying equation (16)

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{H^+} \cdot a_{Fe^{++}}}{a^{\frac{1}{2}}_{H_2} \cdot a_{Fe^{+++}}}; \tag{24}$$

but since for H_2, H^+ ($a = 1$), the voltage is taken as zero, $\frac{RT}{nF} \ln \frac{a_{H^+}}{a^{\frac{1}{2}}_{H_2}}$ is zero, and accordingly $\frac{a_{H^+}}{a^{\frac{1}{2}}_{H_2}}$ must be 1.

Then

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{Fe^{++}}}{a_{Fe^{+++}}}. \tag{25}$$

E^0 is the electromotive force of an inert electrode surrounded by equal quantities of ferrous and ferric ions when measured against the normal hydrogen electrode, for when $a_{Fe^{++}}$ and $a_{Fe^{+++}}$ are equal, the last term becomes zero.

Peters* first demonstrated the applicability of equation (25), and his results are given in the following table. Tenth-normal solutions of ferrous chloride and ferric chloride were mixed in varying proportions and the potential of a platinum wire in the mixture was measured against a reference electrode through a potassium chloride bridge. The solutions were made tenth-normal with respect to hydrochloric acid to prevent hydrolysis.

The values of E^0 are computed on the assumption that the ratio of the concentrations of ferrous and ferric chlorides may be substituted for the ratio of the activities, an assumption which is only approximately correct, but the total ion concentration is constant and it will be observed that the values in the third column are fairly constant.

Popoff and Kunz† have investigated this system more fully, extrapolating to zero concentration of iron and zero concentration of

* Z. physik. Chem., **26**, 193 (1898).

† J. Am. Chem. Soc., **51**, 382 (1929).

FERRI-FERRO POTENTIALS

Ratio Fe^{+++} : Fe^{++} Per cent	Obs. E.m.f. (*N*. Hydrogen Electrode = 0)	Normal Oxidation Potential, E^0	Equilibrium Constant $\frac{c_{Fe^{++}}}{c_{Fe^{+++}}} = K$
0.5 : 99.5	+0.580	0.712	
2 : 98	+0.615	0.712	
10 : 90	+0.655	0.710	
30 : 70	+0.690	0.711	Mean value 10^{12}
40 : 60	+0.702	0.712	
50 : 50	+0.713	0.713	
80 : 20	+0.747	0.712	
90 : 10	+0 762	0.707	

hydrochloric acid. They obtained a series of values of E^0 in progressively more dilute solutions of ferrous and ferric chloride and extrapolated to infinite dilution of iron chlorides. This extrapolated value of E^0 in $N/10$ hydrochloric acid is 0.731, and it may be considered an accurate value obtained with activities instead of concentrations, under conditions where the junction potential is practically eliminated. There is a complication, however, in that the hydrochloric acid changes the character of the solution and affects the value of E^0. A value of 0.747 for E^0 in pure water was obtained by determining the extrapolated value of E^0 in solutions of different normality with respect to hydrochloric acid and extrapolating these values to zero concentration of hydrochloric acid.

In general

$$E = E^0_{(ic \rightarrow ous)} - \frac{RT}{n\bar{F}} \ln \frac{a_{(ous)}}{a_{(ic)}}; \qquad (26)$$

E denotes the electromotive force necessary to transfer an electron from the "ic" or higher state of oxidation to the "ous" or lower state of oxidation, and n denotes the difference in valence of the two ions. A table of normal reduction potentials, E^0, referred to the hydrogen electrode, has been compiled, as shown in the following table. As usual the sign of the electrode potential is determined by placing the normal hydrogen electrode at the left and considering the cell to have a positive voltage when negative electricity flows from right to left inside the cell, and writing the electrode reaction as that reaction which causes negative electricity to flow from right to left within the cell.

NORMAL REDUCTION POTENTIALS

Electrode	Electrode Reaction	Normal Electrode Potential, E^0 (Normal Hydrogen Electrode = 0)
$(Cr^{+++}, Cr^{++})Pt$	$Cr^{+++} + e = Cr^{++}$	−0.400
$(Ti^{++++}, Ti^{+++})Pt$	$Ti^{++++} + e = Ti^{+++}$	+0.04
$(Sn^{++++}, Sn^{++})Pt$	$Sn^{++++} + 2\,e = Sn^{++}$	+0.13
$(Fe^{+++}, Fe^{++})Pt$	$Fe^{+++} + e = Fe^{++}$	+0.7477
$(Hg^{++}, Hg_2^{++})Pt$	$Hg^{++} + e = \frac{1}{2}\,Hg_2^{++}$ *	+0.901
$(Tl^{+++}, Tl^{+})Pt$	$Tl^{+++} + 2\,e = Tl^{+}$	+1.211
$(Ce^{++++}, Ce^{+++})Pt$	$Ce^{++++} + e = Ce^{+++}$	+1.55
$(Co^{+++}, Co^{++})Pt$	$Co^{+++} + e = Co^{++}$	+1.817

* There is evidence that the mercurous ion is doubled, giving not Hg^{+} but $\frac{1}{2}\,Hg_2^{++}$.

Any electrolyte in the reduced or "ous" state (at unit activity) will reduce any electrolyte in the oxidized or "ic" state (at unit activity) which is lower in the table. Any combination of electrodes may be made and from the corresponding voltage the equilibrium constant may be calculated. For example, ferrous chloride will reduce mercuric chloride. Moreover, the ratio of concentrations when equilibrium is attained can be calculated by arranging the following cell, which contains each of the ions at unit activity.

$$\overset{e\longrightarrow}{\underset{\longleftarrow e}{Pt(Fe^{+++},\ Fe^{++})\ ||\ (Hg^{++},\ Hg_2^{++})Pt}}$$

The cell reaction is

$$Fe^{++} + Hg^{++} \rightarrow Fe^{+++} + \tfrac{1}{2}\,Hg_2^{++}$$

$$E^0 = E^0_{Pt(Fe^{+++},\ Fe^{++})} + E^0_{(Hg^{++},\ Hg_2^{++})Pt}$$

$$= -0.7477 + 0.9010 = 0.1533$$

and applying equation (15), at 25°

$$E^0 = 0.1533 = 0.059 \log K$$

$$K = \frac{a_{Fe^{+++}} \cdot a^{\frac{1}{2}}_{Hg_2^{++}}}{a_{Fe^{++}} \cdot a_{Hg^{++}}} = 400$$

This calculation shows that the ferrous ion reduces the mercuric ion to such an extent that, at equilibrium, the product of the activity of the ferric ion by the square root of the activity of the mercurous ion (Hg_2^{++}) is 400 times as great as the product of the activities of the ferrous and mercuric ions.

Normal Electrode Potentials. As already explained, the tendency of a metal to detach electrons and go into solution in the ionic form is measured by the single electrode potential of the electrode against a solution of its ions. Since this potential changes with the concentration of the ions it is necessary to adopt some standard concentration and the *normal electrode potential* is defined as the potential of a metal when immersed in a solution of its ions at unit activity (i.e., effective concentration of 1 gram-ion per 1000 grams of solvent). In most work at the present time this potential is referred to the normal hydrogen electrode potential as zero. The electrode must be reversible of course.

These normal electrode potentials may be considered as a special case of oxidation-reduction potentials for they involve the same type of electron transfer. For example, the reaction corresponding to the zinc electrode is

$$Zn^{++} + 2\,e = Zn$$

and the zinc ions are reduced to zinc atoms by the addition of electrons in the same way that Fe^{+++} ions are reduced to Fe^{++} ions by the gain of electrons.

The relation between the normal electrode potential E^0 and the potential of the electrode E in a solution of its ions at any activity or effective concentration a is obtained with the help of the fundamental equation (16), given on p. 436. Applied to the particular case of an electrode of metal M immersed in a solution of M^+ ions of activity a_{M^+} and connected to a normal hydrogen electrode, the cell is

$$H_2(p = 1 \text{ atmos.}),\ H^+(a = 1) \mid M^+,\ M.$$

The reaction is

$$\tfrac{1}{2}\,H_2 + M^+ = H^+ + M$$

and equation (16) becomes

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{H^+} \cdot a_M}{\sqrt{a_{H_2}} \cdot a_{M^+}}. \tag{27}$$

Since the activities of the hydrogen ion, the hydrogen gas at atmospheric pressure and the solid metal are all permanently fixed and arbitrarily assigned a value of unity, equation (27) becomes

$$E = E^0 - \frac{RT}{nF} \ln \frac{1}{a_{M^+}}, \tag{28}$$

or

$$E = E^0 + \frac{RT}{nF} \ln a_{M^+}. \tag{29}$$

The normal electrode potentials of several elements referred to the hydrogen electrode are given in the following table. A negative sign indicates that the electrode is negative to a solution of its ions at unit activity when the electrode is connected to normal hydrogen electrode.

NORMAL ELECTRODE POTENTIALS AT 25°*

Electrode	E_0 (Normal Hydrogen Electrode = 0)	Electrode Reaction
Li^+, Li	−2.9595	$Li^+ + e = Li$
K^+, K	−2.9241	$K^+ + e = K$
Na^+, Na	−2.7146	$Na^+ + e = Na$
Zn^{++}, Zn	−0.7618	$Zn^{++} + 2e = Zn$
Fe^{++}, Fe	−0.441	$Fe^{++} + 2e = Fe$
Cd^{++}, Cd	−0.4013	$Cd^{++} + 2e = Cd$
Tl^+, Tl(Hg)	−0.3360	$Tl^+ + e = Tl$
Sn^{++}, Sn	−0.136	$Sn^{++} + 2e = Sn$
Pb^{++}, Pb	−0.122	$Pb^{++} + 2e = Pb$
$(H^+, H_2)Pt$	0.0000	$H^+ + e = \frac{1}{2} H_2$
Cu^{++}, Cu	+0.3441	$Cu^{++} + 2e = Cu$
$(I^-, I_2)Pt$	+0.5345	$\frac{1}{2} I_2 + e = I^-$
Ag^+, Ag	+0.7978	$Ag^+ + e = Ag$
Hg_2^{++}, Hg	+0.7986	$Hg_2^{++} + 2e = 2\,Hg$
$(Br^-, Br_2)Pt$	+1.0648	$\frac{1}{2} Br_2 + e = Br^-$
$(Cl^-, Cl_2)Pt$	+1 3583	$\frac{1}{2} Cl_2 + e = Cl^-$
Saturated calomel electrode	+0.2464	
Normal calomel electrode	+0.2805	
Deci-normal calomel	+0.3360	

The reduced form of any element in this table will reduce the oxidized form of any element which occurs below it, provided the materials involved are at unit activity. For example, any positive ion is reduced to the metallic form by taking on electrons from a metal which is higher in the electromotive force series.

Normal electrode potentials and normal reduction potentials are useful in the calculation of the potentials of cells and the free energies of reactions for which direct experimental measurements are not available.

As an example, the possibility of oxidizing ferrous ion to ferric ion with iodine may be determined by calculation of the potential of a cell for which the reaction is $Fe^{++} + \frac{1}{2} I_2 \rightarrow Fe^{+++} + I^-$.

* A change in the order ion-electrode or electrode-ion causes a reversal of the sign. However when two different ions surround one electrode as in the table on p. 440 the order in which the ions are written with respect to each other has no significance. Thus it is immaterial whether the cell is written $(Cr^{+++}, Cr^{++})Pt$, or $(Cr^{++}, Cr^{+++})Pt$; but the sign is reversed by writing $Pt(Cr^{++}, Cr^{+++})$.

Following the conventions, such a cell would be

$$\mathrm{Pt(Fe^{+++},\ Fe^{++})\ ||\ I^-,\ I_2}$$

$$E^0 = E^0{}_{\mathrm{Pt(Fe^{+++},\ Fe^{++})}} + E^0{}_{(\mathrm{I^-,\ I_2})}$$

$$= -0.7477 + 0.5345 = -0.2132$$

$$\Delta F^0 = -nFE^0 = -1 \times 23060 \times (-0.2132) = 4920 \text{ cal.}$$

The positive value of ΔF^0 (or negative value of E^0) indicates that the reaction will not go spontaneously, i.e., solid iodine will not react with ferrous ion at unit activity to produce ferric ion at unit activity and iodide ion at unit activity.

The potential of a reaction is the sum of the potentials of the electrode reactions, and the free energy of a reaction is the sum of the free energies of the electrode reactions. Multiples of the reaction may be taken without changing the potential, but the free energy is changed due to the factor n in the equation $\Delta F = -nFE$.

Thus for the reaction

$$2\ \mathrm{Fe^{++}} + \mathrm{I_2} \rightarrow 2\ \mathrm{Fe^{+++}} + 2\ \mathrm{I^-}$$

$$E = -0.2132 \quad \text{and} \quad \Delta F = 9840 \text{ cal.}$$

and n is the number of faradays transferred through the cell by the reaction.

The Nernst Electrode Equation. The formulas for electrode potentials have been developed in earlier sections through the concepts of thermodynamics and the simple relation between free energy and the mass law. They have been made exact formulas by using *activities* which are defined so as to make the formulas exact. Such a development is useful and logical, but as in all thermodynamical calculations it gives us no insight into the mechanism of the process. In 1889 Nernst proposed a mechanism for the potential of the single electrode, which was of great importance in the early development of electrochemistry.

According to this theory, the atoms of an electrode have a definite tendency to go into solution as ions, and the ions in solution have a definite tendency to deposit out on the electrode as atoms. The former is determined by an imaginary pressure, called the *electrolytic solution pressure* P, and the latter is determined by the effective concentration of ions which, in dilute solutions, is proportional to the osmotic pressure p of the solution.

It is evident that the three following conditions illustrated in Fig. 133 are possible:

(1) If $P > p$, the metal will continue to send ions into the solution until the accumulated charges in the solution oppose further action. The solution acquires a positive charge, and the metal a negative charge.

(2) If $P < p$, the positive ions of the dissolved salt will separate on the metal until the accumulated charges oppose further action. The metal acquires a positive charge and the solution a negative charge.

(3) If $P = p$, no action will take place and no difference of potential will be established between the metal and the solution.

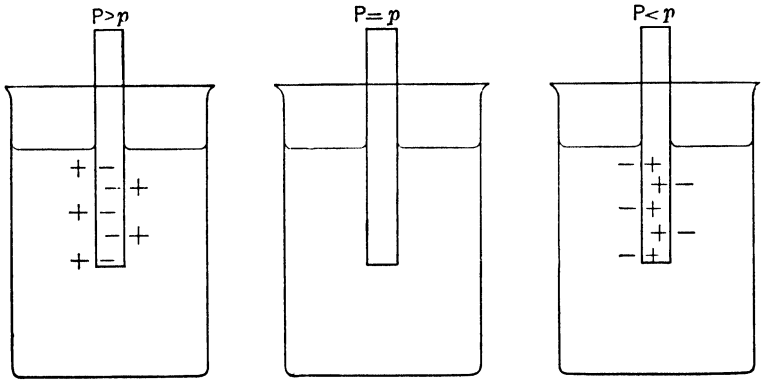


FIG. 133

When equilibrium is established, with an electrode for which $P > p$, the metal is negative against the solution, and is surrounded by a layer of positively charged ions. This constitutes what is known as a Helmholtz *electrical double layer*. If electrons are withdrawn from the metal through an electrical circuit, the double layer will be broken, and more ions will pass from the metal into the solution, but as soon as the removal of electrons is stopped, the double layer will again be formed. Similarly, when the metal is positive against the solution, an electrical double layer will be formed, the metal being surrounded by a layer of negatively charged ions.

The actual existence of a Helmholtz double layer has been demonstrated by Palmaer.* In his experiments exceedingly minute globules of mercury were allowed to fall into a dilute solution of mercurous nitrate, contained in a tall vessel, the bottom of which was covered with pure mercury. The solution became more concentrated at the bottom and in some cases the concentration in the upper part of the solution was reduced as much as 50 per cent. Palmaer explained these

* Z. physik. Chem., **25**, 265 (1898); **36**, 664 (1901).

results by assuming that the mercury globules acquire a positive charge in accord with this theory and drag down with them negative nitrate ions. When the globules are absorbed into the layer at the bottom, the positive charges are given up and mercury ions, equal in number to the nitrate ions brought down, pass into solution.

Nernst developed a thermodynamical cycle in which ions are transferred from a solution of osmotic pressure p to a solution equal in osmotic pressure to the electrolytic solution pressure P. The transfer can be effected by the passage of an electrical current and also by the osmosis of the solvent, each process being carried out reversibly. The work done in the first case is nFE, where E is the potential difference between the two solutions (which form a concentration cell), and the work done in the second case is $\int_P^p RT\, dp/p$, or $RT \ln p/P$. These two expressions are equal because the work done in each case is maximum work, and

$$E = \frac{RT}{nF} \ln \frac{p}{P}. \tag{30}$$

Since no work is involved in transferring the ions from the solution at pressure P to the electrode at the same pressure, this formula gives the potential of an electrode in terms of its electrolytic solution pressure and the osmotic pressure of the solution of its ions in which it is placed. Then, at 25°,

$$E = \frac{RT}{nF} \ln \frac{p}{P} = \frac{0.059}{n} \log \frac{p}{P}. \tag{31}$$

If two electrodes of the same metal are immersed in two solutions of osmotic pressures p_1 and p_2, the voltage of the concentration cell thus formed is given by the equation

$$E = E_1 + E_2 = \frac{0.059}{n} \log \frac{P}{p_1} + \frac{0.059}{n} \log \frac{p_2}{P} = \frac{0.059}{n} \log \frac{p_2}{p_1}. \tag{32}$$

The Nernst equation (30) provides a qualitative interpretation of electrode potentials but it cannot be quantitatively tested because the absolute values of E and P are not known. The electrolytic solution pressure cannot be measured directly, and in calculating it from electrode potentials the value depends entirely on the arbitrary choice of the normal hydrogen electrode or other electrode for the reference standard. In all practical work the electrolytic solution pressure cancels out and the formulas are equivalent to those which have been derived before, without making use of this hypothetical quantity.

Concentration Cells. We now proceed to consider cells in which the electromotive force depends primarily on differences in concentration; of these there are two types.

(a) *Cells in which the Electrodes are of Different Concentrations.* Let us consider a concentration cell formed by two amalgams containing different concentrations of the same metal M immersed in a solution of the metal ions M^+,

$$M(a_2),\ M^+,\ M(a_1). \qquad a_2 > a_1 \qquad (33)$$
$$\longleftarrow e$$

The free energy decrease involved in diluting the concentrated amalgam having an activity a_2 to the dilute amalgam having an activity a_1, is given by the equation

$$-\Delta F = w = RT \ln \frac{a_2}{a_1}. \qquad (34)$$

The dilution may be effected also by connecting the electrodes with a wire and allowing a current to pass. The free energy decrease is given by the equation

$$-\Delta F = w = nFE. \qquad (35)$$

Combining these two equations

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1}. \qquad (36)$$

Since in dilute solutions the concentrations may be substituted for activities,

$$E = \frac{RT}{nF} \ln \frac{c_2}{c_1}. \qquad (37)$$

The approximate accuracy of this equation has been established by the experiments of Meyer* on dilute amalgams.

Meyer's results for zinc amalgams in solutions of zinc sulphate are given in the accompanying table.

E.M.F. OF ZINC AMALGAMS

T, degrees	c_2	c_1	E (obs.)	E (calc.)
284.6	0.003366	0.00011305	0.0419	0.0416
291.0	0.003366	0.00011305	0.0433	0.0425
285.4	0.002280	0.0000608	0.0474	0.0475
333.0	0.002280	0.0000608	0.0520	0.0519

* Z. physik. Chem., **7**, 477 (1891).

The agreement between the observed and calculated values of E is good. That the above formula holds for zinc amalgams may be considered as a proof that zinc dissolves in the mercury as monatomic molecules. Thus, if the zinc were present in the mercury in the form of diatomic molecules, the electrical energy would be equal to $2\,nFE$ and the observed value of the electromotive force would be just one-half the above calculated value. The mercury in the amalgam has been shown to exert no effect upon the electromotive force of the cell, so long as the dissolved metal has a more negative potential than has the mercury.

More recent investigations show that equation (37) does not hold at all in more concentrated amalgams.* If for example some of the dissolved metal combines with the mercury, it is not all available for direct ionization and the concentrations c are not equal to the activities a.

Similar concentration cells can be arranged in which the electrodes are gas electrodes at different partial pressures, p_2 and p_1. The activities of the electrodes are proportional to the partial pressures of the gas, thus

$$\underset{\longleftarrow e}{H_2(p_2),\ H^+,\ H_2(p_1)} \qquad p_2 > p_1 \tag{38}$$

and

$$E = \frac{RT}{nF} \ln \frac{p_2}{p_1}. \tag{39}$$

(b) *Cells in which the Solutions are of Different Concentrations.* In this type of cell we have two electrodes of the same metal immersed in solutions of different ionic activities a_1 and a_2. Thus

$$\underset{\longleftarrow e}{\overset{e\longrightarrow}{M,\ M^+\ (a_1)\ ||\ M^+\ (a_2),\ M.}} \qquad a_2 > a_1 \tag{40}$$

The maximum work done in diluting from a_2 to a_1 is $RT \ln a_2/a_1$, and the maximum electrical work done in effecting the same dilution is given by $-\Delta F$ or nFE. Then

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1}, \tag{41}$$

where E is the electromotive force of the concentration cell.

Molal concentrations m may be substituted for the activities a by

* Richards and Daniels, J. Am. Chem. Soc., **41**, 1732 (1919).

introducing the activity coefficients γ which are defined in the following section according to the relation

$$a = m\gamma.$$

Then,
$$E = \frac{RT}{nF} \ln \frac{m_2\gamma_2}{m_1\gamma_1}. \tag{42}$$

In very dilute solutions the activity coefficients γ become unity and the effective concentrations a become identical with the analytically determined concentrations c or m

and
$$E = \frac{RT}{nF} \ln \frac{m_2}{m_1} = \frac{RT}{nF} \ln \frac{c_2}{c_1}. \tag{43}$$

As an example of a concentration cell of this type we may take the following:

$$\text{Ag, } 0.01\ m\ \text{AgNO}_3 \,||\, 0.1\ m\ \text{AgNO}_3\text{, Ag} \qquad \longleftarrow e \tag{44}$$

The activity coefficients γ at 18° are 0.93 for 0.01 m $AgNO_3$ and 0.81 for 0.1 m $AgNO_3$.

Substituting in equation (42)

$$E = .058 \log \frac{m_2\gamma_2}{m_1\gamma_1} = .058 \log \frac{0.1 \times 0.81}{0.01 \times 0.93} = 0.0545 \text{ volt.} \tag{45}$$

The value of E, found by direct experiment, is 0.055 volt.

Ionization and Activity. The term *activity* may be defined as that quantity which, when substituted for the concentration of a given substance in the mass-action equation, will express its effect in determining the equilibrium. The simple equations which apply only in dilute solutions may be made applicable also to concentrated solutions by substituting activities, or effective concentrations, for analytically determined concentrations. A similar situation was met with on p. 274. This simple artifice is not quite as fundamental as it might appear at first sight, for a new and unknown variable, the activity coefficient γ, has been introduced. However, this activity coefficient may be determined experimentally in a number of different ways (in terms of appropriate conventions) and it is a great advantage to be able to use such equations with exactness even if the evaluation of the new quantity is sometimes rather difficult. Specific methods for determining activities will be given in Chapter XIX.

In the case of dilute solutions of weak electrolytes, like acetic acid, the activity coefficient γ is very nearly equal to the conductance ratio or "degree of dissociation" α calculated from conductance measurements. It was shown on p. 381 that under these conditions $\alpha = \Lambda/\Lambda_0$.

This formula has been extended to strong electrolytes, but it now appears that such an extension is not justified on theoretical grounds because in some cases the electrolyte is 100 per cent dissociated, and in all cases the variation of conductance with concentration is complicated by interionic attraction. This interionic attraction influences the mobility of the ions and affects the conductance of the solution. By pulling the ions together it also affects the concentration at a surface, leading on the one hand to an abnormal vapor pressure, and freezing-point depression, and on the other hand to an abnormal electrode potential. The effect on conductance is not necessarily the same as on the other properties, but consists in a retarding of the motion of ions through the solution. Sometimes in the absence of exact data on the activity coefficient γ, the conductance ratio α may be used as a *first approximation.*

These effects are clearly shown for solutions of potassium chloride in the following table where the ratios of analytically determined concentrations are given in the first column, the ratios based on conductance measurements in the second column, and the activities, as determined from electromotive force measurements, in the third column.

RATIOS OF ION CONCENTRATIONS IN SOLUTIONS OF POTASSIUM CHLORIDE

c_2/c_1 (Concentration Ratio)	$m\alpha_2/m\alpha_1$ (Conductance)	a_2/a_1 (Electromotive Force)
0.5 : 0.05	8.85	8.09
0 1 : 0.01	9.16	8.33
0.05 : 0.005	9.30	8.64
0.01 : 0.001	9.62	9.04

The activity of a uni-univalent electrolyte may be defined as the product of the ionic activities,

$$a_+ \cdot a_- = a_{\text{solute}}. \tag{46}$$

The *mean activity*, $a_\pm$, of the solute is then defined by the equation

$$a_\pm = (a_+ \cdot a_-)^{\frac{1}{2}}, \tag{47}$$

and the *activity coefficient*, γ, is defined as the mean activity product of the ions divided by the molal concentration of the electrolyte. The activity coefficient of a uni-univalent electrolyte will be, therefore,

$$\gamma = \frac{a_\pm}{m} = \left(\frac{a_+ \cdot a_-}{m^2}\right)^{\frac{1}{2}}, \tag{48}$$

or, in words, it is equal to the square root of the product of the activity coefficients of the ions.

In dilute solutions it may be considered that $a_+ = a_- = a_\pm$ and the ionic activities may be approximated by the relation

$$a = m\gamma \tag{49}$$

where a is an ionic activity (a_+ or a_- depending upon the cell in question).

An equation involving both ions, similar to equation (41) for a single ion, may be written in the form

$$E = \frac{RT}{nF} \ln \frac{a''_+ \cdot a''_-}{a'_+ \cdot a'_-} \tag{50}$$

where the single and double accents denote the activities of the solute at two different concentrations. This equation applies only to cells in which the electrodes are reversible with respect to both cation and anion.

Since $(a_+ \cdot a_-)^{\frac{1}{2}} = m\gamma$, it follows that equation (50) may be written in the form,

$$E = \frac{2\,RT}{nF} \ln \frac{m''\gamma''}{m'\gamma'}, \tag{51}$$

which, at 25° C., becomes, on passing to Briggsian logarithms,

$$E = 0.1183 \log \frac{m''\gamma''}{m'\gamma'}. \tag{52}$$

The activity coefficient at infinite dilution is defined as unity. If m' is exceedingly small γ' is 1, and γ'' may be obtained from equation (52) when E and m'' are known. It is impractical to make measurements in such dilute solutions and so it is necessary to extrapolate E as some function of m to infinite dilution (p. 516). In this manner the activity coefficients given in the following table have been determined.

It will be noted that the activity coefficients of these electrolytes pass through a distinct minimum value but that the minima do not occur at the same concentration for each solute. The activity coefficients of three uni-univalent chlorides are plotted against their concentrations in Fig. 134. These curves not only reveal the presence of minima in the values of the activity coefficients, but also they show that the latter are greater in those solutions whose cations possess high hydration values.

Usually the activity coefficients are less than 1 and the effective concentration is less than the analytically determined value. Sometimes, as in the case of concentrated solutions of hydrochloric acid or in non-aqueous solutions, the activity coefficients are found to be much

ACTIVITY COEFFICIENTS AT 25° C.

c	KCl	KBr	NaCl	LiCl	KOH	HCl
0 001	0.965	0.965	0.966	0.965	0.965	0.965
0 01	0 899	0.903	0.903	0.901	0.920	0.904
0.05	0.815	0.816	0.821	0.819	0.822	0.829
0.1	0.764	0.765	0.778	0.779	0.792	0.796
0.2	0.712	0.715	0.732	0.756	0.763	0.766
0.5	0.644	0.653	0.678	0.725	0.740	0.757
1	0.597	0.612	0.656	0 757	0.775	0.810
2	0.569	0 589	0.670	0.919	.....	1.019
3	0.571	0.590	0 714	1.174	1.136	1.320
4	0.581	0.609	0.779	1.554	.....	1.762
5	.....	.....	0.892	.....	.....	.....
6.12	.....	.....	1.019 (sat.)	.....	.....	.....

greater than 1. It is of doubtful value to offer a mechanism for activities, but this effective concentration, so much greater than the stoichiometric concentration, may be attributed to a change in the

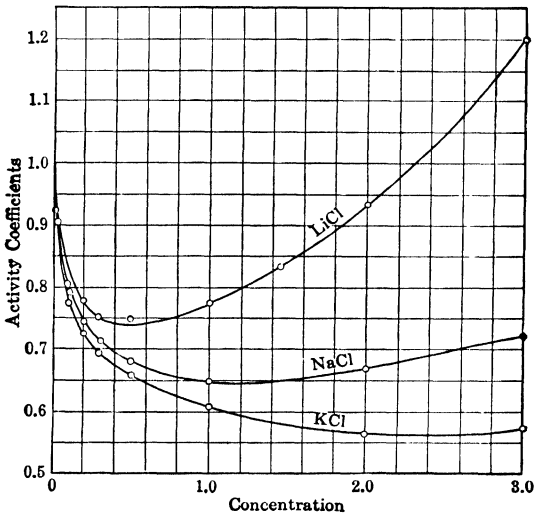


FIG. 134

solvent. The effective concentration may be increased by removing solvent quite as well as by increasing the amount of dissolved solute. As shown in Fig. 77 (p. 204), lithium chloride, which crystallizes out with water of crystallization, may very likely render some of the water inactive as a solvent and thereby make the effective concentration

greater in concentrated solutions, than the analytically determined concentration. In very concentrated hydrochloric acid solution the high value of the activity coefficient γ is probably due to the presence of hydrochloric acid molecules which are absent in dilute solutions.

The activity coefficients of a large number of electrolytes, both alone and mixed, in solutions of varying concentrations have been determined with a high degree of accuracy.*

The Difference of Potential at the Junction of Electrolytes. Thus far we have not taken into consideration the potential differences which may be established at the junction of two solutions. Nernst has shown that in many cases it is possible to calculate these differences of potential by means of his osmotic theory of the origin of electromotive force, and the values thus obtained are in close agreement with the results of experiment. Let us imagine that two solutions of hydrochloric acid of different concentrations are brought together so as to avoid mixing, the acid in each solution being highly ionized. The hydrogen and chlorine ions will diffuse independently, and since the former move with the greater velocity, the more dilute solution will soon contain an excess of H^+ ions and the more concentrated solution an excess of Cl^- ions. The more dilute solution will become positively charged, owing to the presence of an excess of H^+ ions, while the more concentrated solution will acquire a negative charge, due to the presence of an excess of Cl^- ions. The accumulation of positive electricity, however, will retard the velocity of the H^+ ions and accelerate the velocity of the Cl^- ions, so that, ultimately, the two ions will move with the same average velocity. The difference of potential produced in this way will cease to exist when the two solutions have acquired the same concentration.

* MacInnes and Parker, J. Am. Chem. Soc., **37**, 1445 (1915); MacInnes and Beattie, Ibid. **42**, 1117 (1920); Beattie, Ibid. **42**, 118 (1920); Pearce and Hart, Ibid. **43**, 2483 (1921); Allmand and Polack, J. Chem. Soc., **115**, 1020 (1919); Ming Chow, J. Am. Chem. Soc., **42**, 488 (1920); Knobel, Ibid. **45**, 70 (1923); Getman, Ibid. **42**, 1556 (1920); Harned, Ibid. **37**, 2460 (1915); **42**, 1808 (1920); **44**, 252 (1922); Harned and Brumbaugh, Ibid. **44**, 2729 (1922); Horsch, Ibid. **41**, 1787 (1919); Lewis and Randall, Ibid. **43**, 1112 (1921); Linhart, Ibid. **39**, 615, 2601 (1917); **41**, 1775 (1919); Loomis, Essex and Meacham, Ibid. **39**, 1133 (1917); MacInnes, Ibid. **41**, 1086 (1919); Noyes and Ellis, Ibid. **39**, 2532 (1917); Noyes and MacInnes, Ibid. **42**, 239 (1920); Randall and Cushman, Ibid. **40**, 393 (1918); Lucasse, Ibid. **48**, 626 (1926); Pearce and Gelbach, J. Phys. Chem., **29**, 1023 (1925); Schreiner, Z. anorg. Chem., **121**, 321 (1922); McKeown, Trans. Faraday Soc., **17**, 517 (1922); Bjerrum, Z. anorg. Chem., **109**, 280 (1920); Z. physik. Chem., **104**, 406 (1923); Corran and Lewis, J. Am. Chem. Soc., **44**, 1673 (1922); Scatchard, Ibid. **47**, 641, 648 (1925); Harned, Ibid. **47**, 676, 684, 689 (1925); Randall and Scott, Ibid. **49**, 647 (1927); Harned, Ibid. **51**, 416 (1929); Taylor's Treatise on Physical Chemistry, pp. 763–825. Additional references are given in Chapter XIX.

In general, it may be stated that the difference of potential set up at the junction of the two solutions is caused by the difference in the rates of migration of the two ions, the more dilute solution acquiring a charge corresponding to that of the faster moving ion.

Electromotive Force of Concentration Cells with Transference. In a concentration cell with metal electrodes let u and v be the migration velocities of the cation and anion, respectively, and let a_2 be the activity of the ions in the concentrated solution and a_1 be the activity of the ions in the dilute solution. Now let the cell operate until one gram molecule of metal has reacted at the electrodes, causing the passage of n faradays of electricity through the solution. Then $\frac{v}{u+v}$ mols of negative ions will have migrated to the negative electrode, i.e., from the concentrated to the dilute solution, since the cell is reversible to positive ions and the electrode in the more dilute solution is the negative electrode. Also $\frac{u}{u+v}$ mols of positive ions will have migrated to the positive electrode, i.e., from the dilute to the concentrated solution. The maximum work done by the process will be

$$\frac{v}{u+v}RT\ln\frac{a_2}{a_1}-\frac{u}{u+v}RT\ln\frac{a_2}{a_1}=\frac{v-u}{u+v}RT\ln\frac{a_2}{a_1}. \tag{53}$$

The corresponding electrical energy developed is nFE_j, where E_j is the potential difference at the junction of the two solutions, and

$$E_j=\frac{v-u}{u+v}\frac{RT}{nF}\ln\frac{a_2}{a_1}. \tag{54}$$

As an example of the use of this formula we may take the calculation of the electromotive force of the following combination:

$$\begin{array}{ccccc} & & e\longrightarrow & & \\ (E_1) & & (E_j) & & (E_2) \\ \mathrm{Ag},\ 0.01\ m\ \mathrm{AgNO_3} & & \vert & & 0.1\ m\ \mathrm{AgNO_3},\ \mathrm{Ag}. \\ (a_1) & & \vert & & (a_2) \\ & & \longleftarrow e & & \end{array} \tag{55}$$

Taking the junctions in order (1), (j) and (2), we obtain the total voltage E of the cell,*

* It will be noted that all the potentials are added together; the signs of the electrode potentials being determined by the convention, and the sign of E_j by the relative magnitudes of u and v and of a_2 and a_1.

$$E = E_1 + E_j + E_2$$

$$= -\left(E^0_{Ag} + \frac{RT}{nF}\ln a_1\right) + \frac{v-u}{u+v}\frac{RT}{nF}\ln\frac{a_2}{a_1} + \left(E^0_{Ag} + \frac{RT}{nF}\ln a_2\right)$$

$$= \frac{RT}{nF}\ln\frac{a_2}{a_1} + \frac{v-u}{u+v}\frac{RT}{nF}\ln\frac{a_2}{a_1}$$

$$= \frac{v+u+v-u}{u+v}\frac{RT}{nF}\ln\frac{a_2}{a_1} = \frac{2v}{u+v}\frac{RT}{nF}\ln\frac{a_2}{a_1}$$

$$= 2n_a\frac{RT}{nF}\ln\frac{a_2}{a_1}. \qquad (56)$$

The transference number for the anion of silver nitrate is 0.522 and

$$a_2 = m_2\gamma_2 = 0.1 \times 0.82 = 0.082$$

and $$a_1 = m_1\gamma_1 = 0.01 \times 0.94 = 0.0094.$$

Hence, at 25° C.,

$$E = 2 \times 0.522 \times 0.059 \times \log\frac{0.082}{0.0094} = 0.058 \text{ volt.}$$

The value found by direct experiment is 0.056 volt.

When applied to cells reversible to negative ions, the electrode in the more dilute solution is the positive electrode and equation (56) takes the form

$$E = 2n_c\frac{RT}{nF}\ln\frac{a_2}{a_1} \qquad (57)$$

where n_c is the transference number of the cation.

It will be observed that the expressions for the potentials calculated in this way contain the transference number of the ion opposite in sign to the ion with respect to which the cell is reversible.

Other formulas have been suggested for calculating the difference in potential E_j at liquid junctions. Assuming that both anion and cation have approximately the same velocity, MacInnes* proposed the following formula for different concentrations of the same salt, where E_t is the voltage of a cell with transference:

$$E_j = E_t(1 - \tfrac{1}{2}n_c). \qquad (58)$$

It involves no assumptions regarding the concentration of the ions.

Lewis and Sargent† proposed an equation for two equally concentrated electrolytes having a common ion. If Λ_1 and Λ_2 are the equiv-

* J. Am. Chem. Soc., **37**, 2301 (1915).

† J. Am. Chem. Soc., **31**, 363 (1909).

alent conductances of the two electrolytes, the value of the liquid junction potential is

$$E_j = \frac{RT}{nF} \ln \frac{\Lambda_2}{\Lambda_1}. \tag{59}$$

With the use of these two equations, it is possible to calculate the junction potential between any two uni-univalent electrolytes to within a few millivolts.

Corrections for Junction Potentials. The difference in potential at the junction of two liquids must be eliminated or corrected in making accurate measurements of electrode potentials. The most convenient way of minimizing this potential is through the use of a salt bridge of potassium chloride connecting the two solutions of different electrolytes.

It is evident from formula (54) that the junction potential is zero when the transport numbers are 0.5. The same conclusion may be drawn from the fact that under these conditions each ion moves with the same velocity and each has the same tendency to give its charge to the more dilute solution. Potassium chloride is used in salt bridges and in the calomel cell, because potassium and chloride ions have about the same transport numbers and the contact potential is reduced to a minimum.

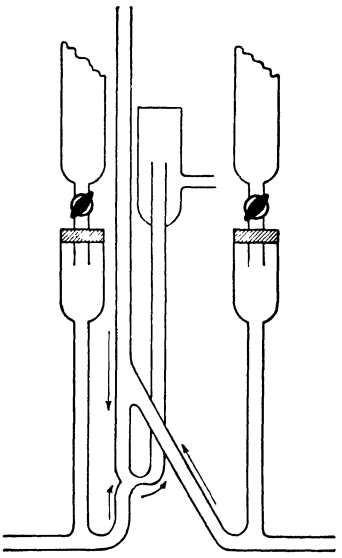


FIG. 135

Other ions than potassium and chloride are usually present at the two ends of the bridge and it is desirable to minimize the effect of these ions by having a large excess of the potassium chloride. For this purpose saturated potassium chloride is more effective than normal potassium chloride but it is more troublesome to use.

The most reproducible junction potentials are obtained with a flowing junction. With the junction of Lamb and Larson* shown in Fig. 135, it is possible to obtain a potential which is constant and reproducible to 0.01 millivolt. An upward current of the denser electrolyte is allowed to meet a downward current of the lighter electrolyte, in a vertical tube at its point of union with a horizontal outflow tube.

* J. Am. Chem. Soc., **42**, 229 (1920).

MacInnes and Yeh,* employing a modified form of the Lamb and Larson flowing junction, have shown that the values of the junction potential, calculated by the formula of Lewis and Sargent (equation 59), are, in nearly every case, in excellent agreement with those found by direct experiment.

The junction potential constitutes one of the most difficult problems in electrochemistry. Apparently it cannot be calculated with the exactness now demanded in electrochemical measurements, and yet it must be known before it is possible to calculate the activity of individual ions. Particularly in the electrochemistry of non-aqueous solutions our ignorance of junction potentials constitutes a serious handicap. According to some workers we can never know the junction potentials and the activities of individual ions.† In some types of cells the liquid junction may be entirely eliminated as shown in the following paragraph.

Electromotive Force of Concentration Cells without Transference. It is possible to set up a combination of half-cells in such a way that there is no boundary between different solutions of the electrolytes. Such a combination of two cells may contain an amalgam in a compartment which is connected with two different solutions as shown in the following combination:

$$\underset{a_1}{\text{Ag, (AgCl, KCl)}}, \text{K(Hg)}_x, \underset{a_2}{\text{(KCl, AgCl) Ag.}}$$

It will be observed that this cell is in reality made up of two independent cells and involves no liquid junction of different electrolytes.

The passage of one faraday of electricity through the cell results in the formation, on the dilute side, of one equivalent of potassium chloride from the silver chloride and the amalgam, while on the concentrated side a corresponding amount of potassium chloride is decomposed. Since the cell is reversible to both ions, equation (50) applies and

$$E = 2\frac{RT}{nF}\ln\frac{a_2}{a_1}. \tag{60}$$

Cells without transference may be arranged with a metallic conductor between the two cells as in the following case:

$$\underset{a_1}{\text{H}_2, \text{HCl, AgCl} + \text{Ag}}, \underset{a_2}{\text{Ag} + \text{AgCl, HCl, H}_2}.$$

Some Applications of Electromotive Force Measurements. (a) *Electrometric Determination of Transference Numbers.* The formula for

* J. Am. Chem. Soc., **43**, 2563 (1921).

† Guggenheim, J. Phys. Chem., **34**, 1758 (1930).

the electromotive force of a concentration cell with transference, and reversible to anions has been shown to be

$$E_t = \frac{2\, n_c RT}{nF} \ln \frac{a_2}{a_1}. \tag{61}$$

If the electromotive force of such a combination is measured and the values of a_1 and a_2 are accurately known, obviously the value of the transference number of the cation, n_c, can be calculated.

It is possible, also, to determine the transference number without involving the concentrations or the activities, for these quantities can be made to cancel out by combining the voltage E_t of a cell with transference with the voltage E of a similar cell without transference which is reversible with respect to both ions.

Dividing equation (61) by equation (60)

$$n_c = \frac{E_t}{E}. \tag{62}$$

The difference between cells with transference and cells without transference must be clearly understood. The cells with transference are reversible with respect to one ion and they are used in an attempt to get information concerning the activity of individual ions. These cells which are reversible with respect to only one ion in the half-cell involve a junction potential which introduces an uncertainty in spite of the use of salt bridges and correcting formulas. Although such cells have great practical value, as for example in the case of the hydrogen electrode, they are not and probably never will be thermodynamically exact.*

The cells without transference are free from this difficulty of the junction potential and are thermodynamically exact, but they are often difficult to devise. Moreover, since they are reversible with respect to both ions the potential of the cell gives the mean activity of both positive and negative ions, and absolute information concerning either one alone is not available.

The transference number of the lithium ion in lithium chloride has been determined in this manner by Pearce and Mortimer,† using cells made up according to the following schemes:

$$\mathrm{Ag} + \mathrm{AgCl},\ \underset{c_1}{\mathrm{LiCl}} \mid \underset{c_2}{\mathrm{LiCl}},\ \mathrm{AgCl} + \mathrm{Ag} \text{ (with transference)},$$

$$\mathrm{Ag} + \mathrm{AgCl},\ \underset{c_1}{\mathrm{LiCl}},\ \mathrm{Li}\ (\mathrm{Hg})_x,\ \mathrm{Li}\ (\mathrm{Hg})_x,\ \underset{c_2}{\mathrm{LiCl}},\ \mathrm{AgCl} + \mathrm{Ag} \text{ (without transference)}.$$

* Guggenheim, J. Phys. Chem., **34**, 1758 (1930).

† J. Am. Chem. Soc., **40**, 518 (1918).

Later determinations of the transference numbers of lithium chloride solutions, by MacInnes and Beattie,* are given in the accompanying table.

TRANSFERENCE NUMBERS OF LITHIUM ION IN LITHIUM CHLORIDE

Concentration	E.m.f. Method 25°	"Best value" Hittorf Method 18°
0.001	0.359	.....
0.005	0.341	.....
0.01	0.334	0.332
0.02	0.327	0.328
0.05	0.318	0.320
0.10	0.311	0.313
0 20	0.304	0.304
0.30	0.299	0.299
0.50	0.293	.....
1.0	0.286	.....
2.0	0.276	.....
3.0	0.268	.....

These results have been shown to be in close agreement with the direct transference measurements of Jahn, Bein, and Washburn.

(b) *Electrometric Determination of Valence.* The equation of Nernst, for the electromotive force of a concentration cell, may be employed to determine the valence of the ions.

For example, the chemical behavior of mercurous salts is such as to justify the use of single or double formulas, involving either Hg^{+} or Hg_2^{++}. To determine which of these two formulas is correct, Ogg† set up the following cell:

$$\text{Hg, } 0.05\ n \text{ Mercurous nitrate} \mid 0.5\ n \text{ Mercurous nitrate, Hg}$$
$$0.1\ n\ HNO_3 \quad \longleftarrow e \quad 0.1\ n\ HNO_3$$
$$c_1 \qquad\qquad c_2$$

and found its electromotive force, at 17°, to be 0.029 volt. If we neglect the difference of potential at the junction of the two solutions, the electromotive force of this cell may be calculated by the familiar formula,

$$E = \frac{RT}{nF} \ln \frac{c_2}{c_1}. \tag{63}$$

* J. Am. Chem. Soc., **42**, 1117 (1920).

† Z. physik. Chem., **27**, 285 (1898).

Assuming that $c_2/c_1 = 10$, and passing to Briggsian logarithms, we have

$$0.029 = 0.058/n,$$

or

$$n = 2.$$

Hence, the valence of the mercurous ion is 2 and it must, in consequence, be represented by Hg_2^{++}. It follows that the correct formula of mercurous nitrate is $Hg_2(NO_3)_2$.

(c) *Solubility Determinations.* The activity or effective concentration of an ion may often be determined by measuring the voltage of a suitable electrode immersed in the solution. From these determinations other properties such as solubility may be calculated, as illustrated with the following data on silver chloride.

Two silver electrodes are arranged in a concentration cell. In one part are silver ions of known concentration and in the other part are silver ions in equilibrium with solid silver chloride:

$$\text{Ag, AgCl (sat.) (0.1 } m\text{), KCl} \mid \text{KNO}_3 \mid \text{AgNO}_3 \text{ (0.1 } m\text{), Ag.} \qquad (64)$$
$$\longleftarrow e$$

The voltage E of this cell was found by Goodwin* to be 0.450 volt at 25° C., and the activity coefficient γ of the 0.1 molal silver nitrate is 0.82, and from equation (42),

$$E = 0.059 \log \frac{m_2\gamma_2}{m_1\gamma_1} \qquad (65)$$

$$0.450 = 0.059 \log \frac{0.1 \times 0.82}{m_1\gamma_1} \qquad (66)$$

$$m_1\gamma_1 = 1.94 \times 10^{-9}. \qquad (67)$$

This solution of silver chloride in equilibrium with solid silver chloride is so dilute that γ_1 may be considered practically 1. The activity coefficient of the 0.1 molal potassium chloride is about 0.85 and the solubility product is then given by the equation

$$s = c_{Ag^+} \times c_{Cl^-} = (1.94 \times 10^{-9}) \times (0.1 \times 0.85) = 1.65 \times 10^{-10}. \qquad (68)$$

When silver chloride is dissolved in pure water, the concentrations of silver ions and chloride ions are the same, and by equation (68), $c_{Ag^+} = \sqrt{s}$ or $\sqrt{1.65 \times 10^{-10}}$ or 1.28×10^{-5}. The solubility of silver chloride is therefore 1.28×10^{-5} mol per 1000 grams of water.

The Hydrogen Electrode. The determination of the effective concentration of hydrogen ions in a solution has been of great practical importance, and the hydrogen electrode has been of inestimable value

* Z. physik. Chem., **13**, 577 (1894).

in such determinations. Hydrogen gas does not conduct the electric current, and it cannot be used alone as an electrode, but when adsorbed on the surface of platinum it behaves just as if it were a metallic electrode and the reaction

$$\tfrac{1}{2}\,H_2 = H^+ + e$$

is completely reversible as shown by laboratory tests and by thermodynamic criteria. Hydrogen ions can apparently break away from the layer of hydrogen atoms adsorbed on the surface and the platinum acts as an inert electrical conductor, without entering the reaction of the cell. To act efficiently the electrode must be covered with platinum black to give a large surface area for adsorption. The electrode

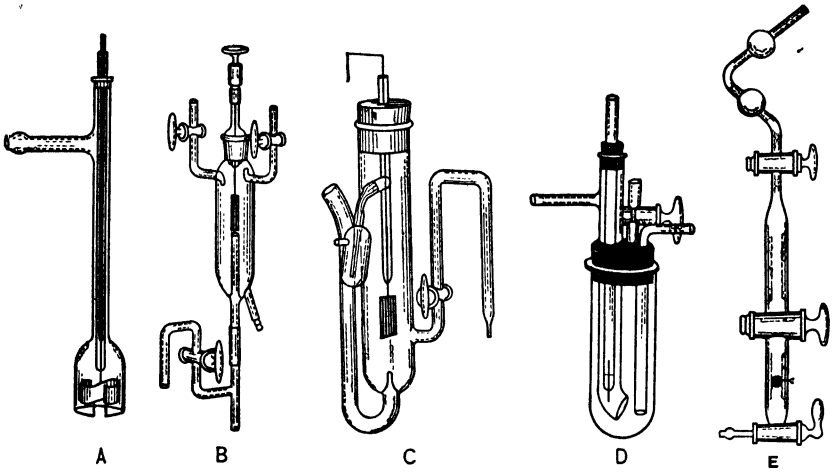


FIG. 136

is arranged in such a way that hydrogen bubbles up around the platinum, or else the electrode is partly immersed in the solution and partly in the hydrogen and the level of the liquid is changed as the gas bubbles out from a glass hood which surrounds the electrode. It is necessary to have the electrode in equilibrium with the solution which is saturated with hydrogen.

Numerous forms of hydrogen electrodes have been devised but those shown in Fig. 136 are among the most satisfactory. In accurate work the hydrogen must be at a definite, known pressure and it must contain no oxygen or air. In some solutions it is not feasible to bubble gas through the cell because the equilibrium of the solution with other gases is upset, as for example, in the case of blood.

Chlorine and some other gases may be used with platinum as gas electrodes in the same way that hydrogen is used. Some gas electrodes, as for example the oxygen electrode, are useful in titrations, but since they are irreversible they are of little theoretical interest. Other gases function merely in stirring the liquid in the neighborhood of the electrode and as a means of changing the relative adsorption of ions. With these electrodes it is not possible to calculate the concentration of the ions from a given e.m.f., but end-points may be determined in titrations.

A hydrogen concentration cell can be formed by connecting two hydrogen electrodes, containing the gas at different pressures, as in the following cell:

$$\underset{\longleftarrow e}{\overset{e\longrightarrow}{H_2(p_2),\ H^+(a_1)\ ||\ H^+(a_1),\ H_2(p_1)}}$$

where $p_2 > p_1$. The direction of the current is such that the pressures on the two sides of the cell tend to become equal, molecular hydrogen being ionized on the high-pressure side and ionized hydrogen being discharged on the low-pressure side. The electromotive force of such a cell may be calculated by means of equation (32)

$$E = E_1 + E_2 = \frac{RT}{nF}\ln\frac{p_2}{a_1^2} + \frac{RT}{nF}\ln\frac{a_1^2}{p_1} = \frac{RT}{nF}\ln\frac{p_2}{p_1}, \qquad (69)$$

where p_2 and p_1 refer to the gas pressures, and a_1 refers to the activity of the hydrogen ions in the cell. Since hydrogen gas is diatomic, n has a value of 2, and the concentrations of the hydrogen ion are squared in accordance with the reaction

$$2\,H^+ + 2\,e = H_2,$$

and

$$E = \frac{RT}{2\,F}\ln\frac{p_2}{p_1}. \qquad (70)$$

Two hydrogen electrodes at the same gas pressure can be used to measure the hydrogen ion activity in a concentration cell, as follows:

$$\underset{\longleftarrow e}{H_2(p = 1),\ H^+(a_1)\ \|\ H^+(a_2),\ H_2(p = 1)} \qquad (71)$$

where $a_2 > a_1$.

$$E = E_1 + E_2 = \frac{RT}{2\,F}\ln\frac{a_2^2}{a_1^2} = \frac{RT}{F}\ln\frac{a_2}{a_1}. \qquad (72)$$

If half of the concentration cell (the one at the left in the cell as written

above) is filled with a solution whose activity of hydrogen ions is 1, then

$$E = \frac{RT}{F} \ln a_2. \tag{73}$$

In practical work it is much easier to use a calomel electrode than a hydrogen electrode and so the normal hydrogen electrode is replaced by a calomel electrode and a corresponding correction is applied. Careful measurements have shown that the normal calomel electrode is positive to the normal hydrogen electrode by 0.281 volt. Then the equation for the voltage of a hydrogen electrode in a solution of hydrogen ions of activity a against a normal calomel cell at 25° C. is given by equation (74) which is obtained as follows:

(1) $(Pt)H_2, H^+(a = 1) \,||\, H^+(a), H_2(Pt)$

$$E_1 = \frac{RT}{F} \ln a = 0.059 \log a.$$

Reversing the order,

(2) $(Pt)H_2, H^+(a) \,||\, H^+(a = 1), H_2(Pt)$

$$E_2 = -0.059 \log a = 0.059 \log \frac{1}{a}.$$

Writing the cell for the normal calomel electrode

(3) $(Pt)H_2, H^+(a = 1) \,||\, KCl\ (1\ N), Hg_2Cl_2, Hg$

$$E_3 = 0.281.$$

Combining cells (2) and (3)

(4) $(Pt)H_2, H^+(a) \,||\, KCl\ (1\ N), Hg_2Cl_2, Hg$

and adding potentials,

$$E = E_2 + E_3 = 0.059 \log \frac{1}{a} + 0.281. \tag{74}$$

This is the working equation for the hydrogen electrode using hydrogen at 1 atmosphere, a normal calomel electrode and a salt bridge of potassium chloride which reduces the liquid junction potential to a minimum. It must be realized that the effective concentrations or activities are given in this formula, but in the very dilute solutions of hydrogen ions which are usually studied the activities and the actual concentrations are practically the same. It must be emphasized also that there is an uncertainty regarding the junction potential which prevents the accurate determination of absolute values of individual ion

activities and that new determinations of activities of acids used in the normal hydrogen electrode may change the value of the constants.

Hydrogen Ion Concentrations. Hydrogen ion activities are commonly expressed by bacteriologists and biochemists in terms of the negative exponents of the actual hydrogen ion activities. Sörensen,* who first proposed this method of expressing hydrogen ion concentration, recommended the symbol P_{H+}, but the subsequent suggestion of Clark† that hydrogen ion concentration be denoted by the symbol pH has been practically universally adopted because of its greater simplicity. The relation of pH to hydrogen ion concentration, as hitherto expressed by the symbol a_{H^+}, is indicated by the equation,

$$p\mathrm{H} = \log \frac{1}{a_{H^+}}, \quad \text{or} \quad a_{H^+} = 1 \times 10^{-p\mathrm{H}}. \tag{75}$$

Equation (74) may be rewritten to give

$$p\mathrm{H} = \frac{E - 0.281}{0.059}. \tag{76}$$

The definition of pH is subject to minor differences among the early workers in this field.

The relation between a_{H^+} and pH may be illustrated with a solution which is 0.001 molal with respect to hydrogen *ions*. In this solution the a_{H^+} is 10^{-3} and the pH is 3. Also in a 0.0002 molal solution a_{H^+} is 2×10^{-4} and the pH is log $1/(2 \times 10^{-4})$ or 3.699.‡

Water dissociates into hydrogen and hydroxyl ions according to the reaction

$$H_2O = H^+ + OH^-$$

and, therefore,

$$\frac{a_{H^+} \times a_{OH^-}}{a_{H_2O}} = K'.$$

Considering the large excess of water to be a constant, the ionic product of water may be written

$$K = a_{H^+} \times a_{OH^-}. \tag{77}$$

The approximate value of K, at 25° C., is 1×10^{-14}. If the normal concentration of hydroxyl ions in water is increased by the addition of

* Sörensen, Biochem. Z., **21**, 131 (1909).

† Clark, " The Determination of Hydrogen Ions."

‡ The calculation may also be made as follows: $p\mathrm{H} = -\log a_{H^+} = -\log (2 \times 10^{-4}) = -(\bar{4} + 0.301) = 3.699$. Further examples of negative logarithms of this type are given in " Mathematical Preparation for Physical Chemistry," p. 11.

a base, the concentration of hydrogen ions will experience a corresponding decrease, in order that the value of the ionic product, K, shall remain constant. Thus, if in the aqueous solution of a base, the activity of the hydroxyl ions is 1×10^{-4}, the activity of the hydrogen ions must be

$$a_{H^+} = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10},$$

or $p\mathrm{H} = 10$. Since at ordinary temperatures, $K = 1 \times 10^{-14}$, we may write

$$p\mathrm{H} + p\mathrm{OH} = 14.$$

The activities of H^+ ions may be thought of as effective concentrations which can be calculated from the product of the known concentration of an acid and the activity coefficient.

The following table, in which are included the approximate values of a_{H^+} and pH for a few solutions of common electrolytes, will help to show the significance of the Sörensen notation, and the difference between H^+ ion activities and molar concentrations.

a_{H^+} AND pH VALUES OF COMMON ACIDS AND BASES

Solute	Conc. Mols per Liter	a_{H^+}	pH
HCl	1.00 M	8.0×10^{-1}	0.10
HCl	0.10 M	8.4×10^{-2}	1.07
HCl	0.01 M	9.5×10^{-3}	2.02
NaOH	1.00 M	0.90×10^{-14}	14.05
NaOH	0.10 M	0.86×10^{-13}	13.07
NaOH	0.01 M	0.76×10^{-12}	12.12
CH_3COOH	0.10 M	1.36×10^{-3}	2.87
NH_4OH	0.10 M	5.4×10^{-12}	11.27

In these calculations the ionic product of water has been taken as 10^{-14} in agreement with the data on p. 415. The ionic product may be determined directly, with two hydrogen electrodes, one immersed in acid and the other in alkali as represented by the cell

$$H_2,\ 0.1\ m\ \mathrm{KOH} \mid 0.1\ m\ \mathrm{KCl} \mid 0.1\ m\ \mathrm{HCl},\ H_2.$$

The electromotive force of this cell is +0.6560 volt* at 25°. The potential at the junction 0.1 m KOH | 0.1 m KCl is −0.0157 volt, and

* Lorenz and Böhi, Z. physik. Chem., 66, 739 (1909).

that at the junction 0.1 m KCl | 0.1 m HCl is -0.0278 volt, hence the true e.m.f. of the cell without liquid junctions is 0.6995 volt at 25°. Introducing this value into the equation

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1},$$

a_2/a_1 is found to be 6.68×10^{11}. The activity coefficient of 0.1 m HCl is 0.796, and the activity of hydrogen ion in 0.1 m KOH is then $a_1 = m_2\gamma_2 a_1/a_2 = 1.21 \times 10^{-13}$. The activity coefficient of 0.1 m KOH is 0.772, and the ionization constant of water is $a_{H^+} \times a_{OH^-} = 1.21 \times 10^{-13} \times 0.0772 = 0.94 \times 10^{-14}$. In pure water

$$a_{H^+} = a_{OH^-} = \sqrt{K} = \sqrt{0.94 \times 10^{-14}} = 0.97 \times 10^{-7}.$$

This value is in excellent agreement with the values obtained by various other methods as shown in the table on p. 415.

Titrations with the Hydrogen Electrode. Since the neutralization of acids and bases is accompanied by changes in the concentration of hydrogen and hydroxyl ions, it is apparent that the hydrogen electrode can be employed in place of an indicator in acidimetric and alkalimetric titrations. The first application of the hydrogen electrode to the titration of acids and bases was made by Böttger,* who showed that the method was applicable to titrations where ordinary indicators fail to give satisfactory results as, for example, in the titration of deeply colored or turbid solutions.

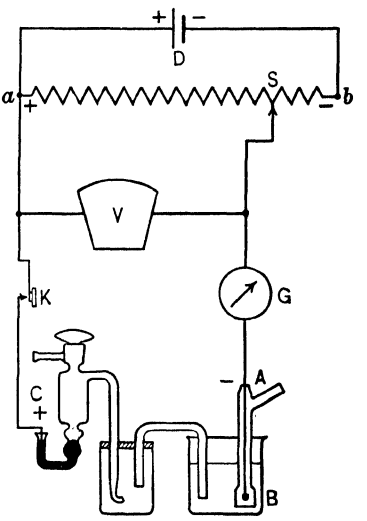


FIG. 137

Subsequently Böttger's method was modified by Hildebrand† who, by substituting a voltmeter for the potentiometer used by Böttger, greatly simplified the procedure of electrometric titration. The arrangement of the apparatus in Hildebrand's method is shown diagrammatically in Fig. 137. The beaker B contains the solution of which the hydrogen ion concentration is sought; into this solution the hydrogen electrode A and the side-tube of a calomel electrode C are introduced. The two electrodes

* Z. physik. Chem., **24**, 253 (1897).

† Hildebrand, J. Am. Chem. Soc., **35**, 847 (1913).

are connected to a battery D through a galvanometer G. The electromotive force of the cell thus formed is balanced against a variable fraction of the electromotive force of the battery D by moving the sliding contact S along the resistance ab until a point is found where, on closing the key K, no deflection is noted on the galvanometer. The voltmeter V serves to indicate the fall of potential from a to S, and, when the point of balance is found, the reading of the voltmeter corresponds to the electromotive force of the cell. Since in a neutral solution, the concentrations of both hydrogen and hydroxyl ions are identical, and equal to 1×10^{-7}, it follows that the end-point of the titration will correspond to a reading on the voltmeter of

$$E = 0.059 \log \frac{1}{1 \times 10^{-7}} + 0.281 = 0.695 \text{ volt.}$$

In carrying out a titration of an acid solution with Hildebrand's apparatus, a solution of standard alkali is run into the beaker B in successive portions from a burette. After the addition of each portion of alkali, the electromotive force of the cell is measured and the reading of the voltmeter plotted against the corresponding burette reading. The amount of alkali required to neutralize the acid is determined by reading from the resulting graph the number of cubic centimeters of standard alkali which corresponds to 0.695 volt.

The results of the titration of hydrochloric and acetic acids by sodium hydroxide are shown graphically in Fig. 138, where the abscissas represent the number of cubic centimeters of sodium hydroxide added to the solution from a burette, and where the ordinates represent the corresponding values of the electromotive force. The scale of hydrogen ion concentrations, at the right of the diagram, is calculated by means of equation (74). It will be seen that, in both cases, a sharp break occurs in the curves when the end-point of the titration is reached.

At the end-point the concentration of hydrogen ions is very small and the number of hydrogen ions in a drop of acid (or of hydroxyl ions in a drop of alkali) is very great in comparison. A slight addition of either acid or alkali then makes a large change in voltage and gives a steep curve. When the solution is already strongly acid or strongly alkaline, the addition of a few more hydrogen or hydroxyl ions from a burette has only a slight effect and the curve is flat.

Acetic acid shows an initial electromotive force much greater than hydrochloric acid, corresponding to the fact that the hydrogen ion concentration is much less. It should be noticed that the first additions of alkali cause a marked decrease in acidity. This shows the

effect of the acetate ion in diminishing the acidity of acetic acid. According to the law of mass action we have,

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+,$$

but the concentration of CH_3COO^- is initially small, owing to the slight ionization of the acid. It is greatly increased by the addition of alkali which forms a salt which is practically completely ionized

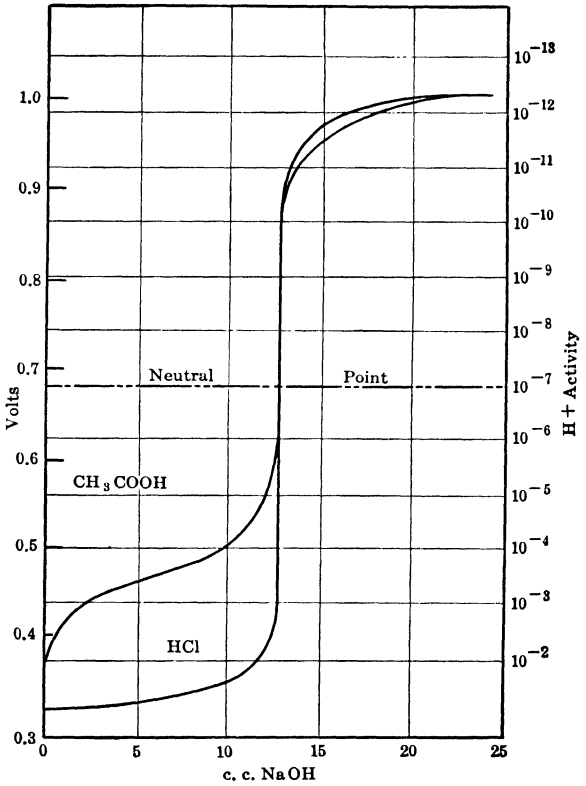


FIG. 138

and the concentration of H^+ ion decreases rapidly. Further addition causes the acidity to decrease very slowly until the neutral point is reached, when a sudden change to alkaline reaction takes place. It can be shown that the middle point of this portion of the curve corresponds to the normal salt, when both acid and base are present in exactly equivalent amounts. It will be observed, however, that this point at which acid and base are equivalent does not correspond to a neutral, but to an alkaline solution. This is in accord with the well-

known fact that sodium acetate solutions are hydrolyzed and give an alkaline reaction.

Similar curves showing the variation in pH on titrating some typical alkaline solutions with hydrochloric acid are plotted in Fig. 139.

It will be noted that there are two end-points in the sodium carbonate curve, the first corresponding to the formation of bicarbonate ion, and the second to that of carbonic acid. The first is represented by the equilibrium

$$CO_3^{--} + H^+ \rightleftarrows HCO_3^-$$

and the second by the equilibrium

$$HCO_3^- + H^+ \rightleftarrows H_2CO_3.$$

It was known empirically, long before these titration curves were obtained, that phenolphthalein is a suitable indicator for the carbonate

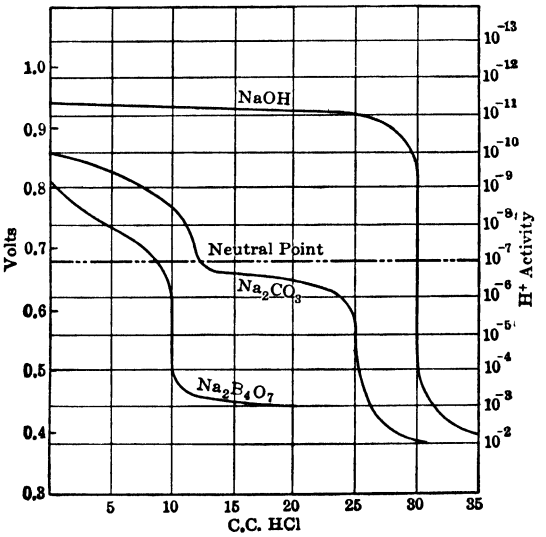


FIG. 139

and methyl orange for the bicarbonate. The former changes color at a pH of about 8 and the latter at about 5, corresponding to the steep parts of the curve, and the reason for this choice of indicators is now evident.

The fundamental difference between hydrogen ion activity as registered by a hydrogen electrode, and the number of cubic centimeters of alkali which are needed to neutralize the acid, should be clearly understood. The latter corresponds to a "reserve" acidity, but the

former gives the actual conditions of acidity and is of fundamental importance in biology and in many chemical processes.

In many of the reactions upon which standard quantitative procedures are based, marked changes in hydrogen ion concentration occur. The feasibility of employing the hydrogen electrode to determine the end-points in many of these reactions was first pointed out by Hildebrand and Harned,* and subsequently the application of the method was further extended by Hildebrand.† For example, it was found that a fairly accurate and rapid determination of magnesia in dolomite could be made in this manner. The curve shown in Fig. 140 represents the results of a typical titration of an acid solution of dolomite with sodium hydroxide. The horizontal distance between the inflections, indicated by the dotted line, *ab*, corresponds to the number of cubic centimeters of standard alkali required to effect the precipitation of the magnesium as hydroxide. The abrupt initial rise in the titration curve corresponds to the neutralization of the excess of acid employed to dissolve the sample of dolomite, together with the amount of alkali required to precipitate the iron.

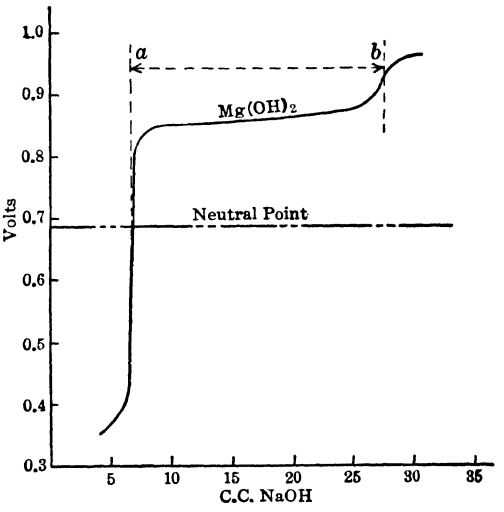


FIG. 140

The hydrogen electrode has proved of great value to the analytical chemist in enabling him to determine the limiting ranges of *p*H which may be employed in both precipitations and separations. As an example of its use in this direction, the investigation of Fales and Ware‡ on the optimum conditions for the precipitation of zinc sulphide may be cited.

Buffer Solutions. If a single drop of 0.1 *m* HCl is added to a liter of pure water, an enormous increase in the hydrogen ion concentration will occur immediately. In like manner, the addition of a drop of 0.1 *m* KOH to a liter of pure water will cause a correspondingly large

* Hildebrand and Harned, Proc. Eighth Internat. Cong. App. Chem., **4**, 217 (1912).

† Hildebrand, J. Am. Chem. Soc., **35**, 847 (1913).

‡ Fales and Ware, J. Am. Chem. Soc., **41**, 487 (1919).

increase in the hydroxyl ion concentration. From these facts it appears that pure water alone is incapable of neutralizing even traces of acids and bases. It is to this lack of reserve neutralizing power that the difficulty of preparing and preserving water having a hydrogen ion concentration of 1×10^{-7} equivalents per liter is to be ascribed.

It has been shown that any solution containing a weak acid together with one of its salts, or a weak base with one of its salts, is capable of neutralizing both acids and bases, within certain limits. This property of certain solutions of resisting change in hydrogen ion concentration, on the addition of acid or alkali, is known as *buffer action*, and the solutions are called *buffer solutions*.

The explanation of buffer action is relatively simple. If to a solution containing a weak acid, HA, and one of its salts, MA, there is added a small amount of an acid or base, the solution will protect itself from a change in pH by neutralizing the added substance according to the following reactions:

$$A^- + H^+ = HA,$$

and

$$HA + OH^- = H_2O + A^-.$$

It follows, therefore, if the reserve acidity is to be equal to the reserve alkalinity, that the concentration of A^- must be equal to the concentration of HA. But, according to the law of mass action,

$$c_{H^+} = \frac{c_{HA}}{c_{A^-}} K_A,$$

hence

$$c_{H^+} = K_A.$$

That is, if the reserve acidity is equal to the reserve alkalinity, the ionization constant of the acid will be numerically equal to the hydrogen ion concentration of the solution.

The pH value of a buffer solution is established by introducing the solution into the beaker B of a cell similar to that shown in Fig. 137, and measuring the electromotive force. The value of pH is then calculated by substituting in equation (76) the value of the electromotive force of the cell, after having applied suitable corrections for junction potential and deviations of hydrogen pressure from normal atmospheric pressure. In this manner the graded pH values of the series of buffer solutions given in the following table were determined.

A number of standard buffer solutions have been described by Sörensen, Palitzsch, Walpole, and Clark and Lubs.* These solutions

* Clark, " Determination of Hydrogen Ions," pp. 69–83.

have been prepared with great care and their hydrogen ion concentrations accurately determined by hydrogen electrode measurements.

These buffer solutions are very useful as standards of definite *p*H values. A solution may be titrated to a definite hydrogen ion concentration by using two hydrogen electrodes: one immersed in the solution and one immersed in the buffer solution. The two solutions are connected with a salt bridge and the two hydrogen electrodes are connected through a galvanometer and tapping key. The titration is continued until the galvanometer registers zero when the circuit is closed, for under these conditions the hydrogen ion activities are the same in the two solutions.

*p*H VALUES OF A SERIES OF TYPICAL BUFFER SOLUTIONS

No. of cc.			No. of cc.		
*p*H	0.2 *m* Na_2HPO_4	0.1 *m* citric acid	*p*H	0.2 *m* Na_2HPO_4	0.1 *m* citric acid
2.2	0.40	19.60	5.2	10.72	9.28
2.4	1.24	18.76	5.4	11.15	8.85
2.6	2.18	17.82	5.6	11.60	8.40
2.8	3.17	16.83	5.8	12.09	7.91
3.0	4.11	15.89	6.0	12.63	7.37
3.2	4.94	15.06	6.2	13.22	6.78
3.4	5.70	14.30	6.4	13.85	6.15
3.6	6.44	13.56	6.6	14.55	5.45
3.8	7.10	12.90	6.8	15.45	4.55
4.0	7.71	12.29	7.0	16.47	3.53
4.2	8.28	11.72	7.2	17.39	2.61
4.4	8.82	11.18	7.4	18.17	1.83
4.6	9.35	10.65	7.6	18.73	1.27
4.8	9.86	10.14	7.8	19.15	0.85
5.0	10.30	9.70	8.0	19.45	0.55

Buffer solutions are widely used as standards in color titrations when it is desired to titrate to a definite *p*H value. The *p*H of a given solution may often be determined by introducing the proper indicator and comparing the color with the colors obtained by adding the indicator to a series of buffer solutions. The *p*H of the solution is the same as that of the particular buffer whose color matches. Tables of suitable indicators have been arranged which cover the whole range of *p*H values.*

* Clark, Determination of Hydrogen Ions, pp. 67–98.

Electrometric Determination of Hydrolysis. One of the most satisfactory methods which we possess for the determination of the degree of hydrolysis of salts depends upon the measurement of the electromotive force of cells made up as follows:

$$H_2, \text{ salt solution} \mid \text{sat. } NH_4NO_3 \mid (n \text{ KCl}, Hg_2Cl_2), Hg.$$
$$\xleftarrow{\qquad e}$$

A saturated solution of ammonium nitrate is interposed between the solutions to diminish the difference of potential at the junction of the solutions. From the measured electromotive force of the cell, the concentration of the hydrogen ion in the solution is determined, and from this the degree of hydrolytic dissociation of the salt can be calculated. The method is especially valuable in cases where the concentration of the hydrogen ion is very small. Unfortunately, the application of the method is restricted to the salts of metals less noble than hydrogen. In other words, it cannot be used to determine the hydrolysis of the salts of metals which would be precipitated upon the platinum electrode. The applicability of the method is further limited by the fact that certain ions, such as Fe^{+++}, NO_3^-, and ClO_3^-, are either wholly or partially reduced by the hydrogen of the hydrogen electrode.

The method has been successfully applied by Denham* to the determination of the hydrolysis of various salts, among which may be mentioned aluminium chloride, aluminium sulphate, nickel chloride, nickel sulphate, cobalt sulphate, and ammonium chloride. As an illustration of the method, we may take the case of ammonium chloride, which dissociates hydrolytically, according to the equation,

$$NH_4Cl + H \cdot OH \rightleftarrows NH_4OH + HCl.$$

Here we have a weak base and a very strong acid, as the products of hydrolytic dissociation. While the ammonium hydroxide may be regarded as practically non-ionized, the hydrochloric acid is to be considered as having undergone complete ionization. If one mol of ammonium chloride is dissolved in v liters of water, and the degree of hydrolytic dissociation is x, then the concentrations of the products of the reaction, ammonium hydroxide and hydrochloric acid, will be x/v. Since the acid is completely ionized, x/v will also represent the concentrations of the hydrogen and chloride ions. Assuming that the active mass of the water remains constant, we have, according to the law of mass action,

$$K_h = \frac{x^2}{v(1-x)},$$

* J. Chem. Soc., **93**, 41 (1908); Z. anorg. Chem., **57**, 361 (1908).

where K_h is the hydrolytic constant. Since v is 32 l., it only remains to determine x/v, or the concentration of the hydrogen ions, in order to be able to calculate K_h. The concentration of the hydrogen ions may then be determined by substituting the electromotive force of the cell, 0.605 volt, in equation (74). Thus

$$\log \frac{1}{c_{H^+}} = \frac{0.605 - 0.281}{0.059},$$

or

$$\log c_{H^+} = -5.48.$$

Hence

$$c_{H^+} = 3.3 \times 10^{-6}.$$

But $c_{H^+} = x/v$, and therefore $x = 3.3 \times 10^{-6} \times 32, = 0.000106.$

The value of the hydrolytic constant is given by the equation

$$K_h = \frac{x^2}{v(1 - x)} = \frac{(0.000106)^2}{32(1 - 0.000106)} = 3.5 \times 10^{-10}.$$

Electrodes for Measuring Hydrogen Ions. The hydrogen electrode described on p. 460 is the standard instrument for measuring hydrogen ion activities, but it is not always suitable. It is readily poisoned and cannot be used in solutions containing mercury or arsenic, for example. It cannot be used in oxidizing solutions containing such substances as ferric chloride, because the hydrogen is oxidized on the surface of the platinized electrode. The bubbling of the hydrogen gas may disturb the equilibrium which one desires to study, as for example, in carbonate solutions or in blood. Colorimetric indicators, also, are not always suitable. On account of the practical importance of measuring hydrogen ion activities under many different conditions, various other electrodes have been devised, and three typical ones will be discussed briefly. Theoretically, any reaction involving hydrogen ions or hydroxyl ions can be used provided a suitable reversible electrode is available.

*The Quinhydrone Electrode.** Hydroquinone is a weak acid dissociating slightly according to the reaction

$$C_6H_4(OH)_2 = C_6H_4O_2^{--} + 2\,H^+.$$

Quinone ($C_6H_4O_2$) may be reduced to hydroquinone ion by the addition of two electrons according to the reaction

$$C_6H_4O_2 + 2\,e = C_6H_4O_2^{--}.$$

* Biilmann, Trans. Farad. Soc., **9**, 57 (1923).

Then the hydroquinone ion combines with hydrogen ion to give hydroquinone. The whole reaction is

$$2\,H^+ + C_6H_4O_2 + 2\,e \rightleftarrows C_6H_4(OH)_2.$$

A platinum wire or other inert electrode placed in the solution acquires a potential depending on the ratio of the oxidized to the reduced form, which in turn is also a measure of the hydrogen ion concentration. The quantitative relation is

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{\text{hydroquinone}}}{a^2_{H^+} \cdot a_{\text{quinone}}}. \qquad (78)$$

It happens that quinone and hydroquinone form an equimolecular chemical compound, $C_6H_4O_2 \cdot C_6H_4(OH)_2$, called quinhydrone which maintains constant and equal concentrations of quinone and hydroquinone and so equation (78) becomes

$$E = E^0_1 + 0.059 \log a_{H^+} \qquad (79)$$

where E^0_1 has been found by experiment to be 0.6990 when E is referred to the normal hydrogen electrode at 25°.

The quinhydrone electrode is very simple and convenient and it is not easily poisoned. It cannot be used in alkaline solutions (above a pH of 8.5) on account of the chemical reaction and oxidation of the hydroquinone, and it may not give very accurate results in strong salt solutions because the "salting out" effect on the hydroquinone and the quinone may not be exactly the same.

*Oxide Electrodes.** Certain metallic oxides of low solubility may be used as hydrogen ion indicators, because the concentration of the hydroxide is kept constant by the presence of the solid phase, and the concentration of the metal ion, which determines the potential of the electrode, is affected directly by the concentration of hydrogen ions. For example, with a bivalent metal M,

$$MO + 2\,H^+ \rightleftarrows M^{++} + H_2O \qquad (80)$$

and

$$K = \frac{a_{M^{++}}}{a^2_{H^+}} \qquad (81)$$

or

$$a_{M^{++}} = K a^2_{H^+}. \qquad (82)$$

From equation (29)

$$E = E^0 + \frac{0.059}{2} \log a_{M^{++}} = E^0 + \frac{0.059}{2} \log K a^2_{H^+} \qquad (83)$$

and absorbing constant terms into a new constant E^0_1,

$$E = E^0_1 + 0.059 \log a_{H^+}. \qquad (84)$$

* Kolthoff and Furman, "Potentiometric Titrations," second edition, p. 224.

The constant E^0_1 is evaluated experimentally from solutions of known hydrogen ion activity.

One of the best of these oxide electrodes is that of antimony which is represented by the cell

$$(Pt)H_2,\ H^+(a = 1) \mid\mid \text{solution},\ Sb_2O_3,\ Sb.$$

The corresponding formula is

$$E = E^0_1 + 0.059 \log a_{H^+} = +0.144 - 0.059\ p\text{H} \qquad (85)$$

between pH 5 and 10, when air is excluded and special precautions are taken to have the stable (cubic) form of oxide.*

The Glass Electrode.† It has been found that a very thin membrane of soda-lime glass separating two solutions gives potentials which depend directly on the hydrogen ion concentrations. The resistance of the glass diaphragm is so great that a sensitive electrometer or electron-tube voltmeter is required to measure the voltages. The membrane is made by blowing out a bulb so thin that it shows interference colors and thrusting against it a tube the end of which is hot enough to stick to the glass. The membrane is mounted in a cell of the following type:

Calomel electrode, solution of known pH, glass membrane, solution of unknown pH, calomel electrode.

The voltage is a logarithmic function of the difference in hydrogen ion activity except for a small "asymmetry potential" due to the glass.‡ The glass electrode is not affected by oxidizing solutions; it can be used in non-aqueous solutions and in cases where the hydrogen electrode cannot be used. Sometimes the pH on one side of the membrane is adjusted by adding acid or alkali until the glass electrode gives zero potential. Under these conditions the pH on the two sides of the membrane is the same, and it can be determined directly with a hydrogen electrode in the reference solution.

The theory of the glass electrode is not yet clear. The membrane may give potentials corresponding to adsorbed hydrogen ions or it may possibly permit hydrogen ions to pass directly through the glass.

Potentiometric Titrations. In preceding sections it has been shown that activities of ions may be calculated from the potentials of suitable electrodes. Examples of titrations with the hydrogen electrode were given on p. 468, but often it is necessary to know only the end-

* Roberts and Fenwick, J. Am. Chem. Soc., **50**, 2125 (1928).

† MacInnes and Dole, Ind. and Eng. Chem., Analyt. Ed., **1**, 57 (1929).

‡ This may be eliminated by substituting a solution of known pH for the unknown solution in the right-hand half of the cell, thus establishing a correction factor.

point in the titrations and the activities are not important. The problem is then much simpler. It is not necessary to use reversible electrodes, and no theoretical calculations are involved. A reagent is added gradually until the voltage changes rapidly with the addition of a slight amount of reagent. Sometimes the voltage change is so great as to be noted directly on a galvanometer, but more often the voltages E, as read on a potentiometer, are plotted against the volume V of reagent added and the steepest part of the curve is located by inspection. Examples were given in Fig. 138 on p. 467. Two or more points of inflection of this type may occur, due to polybasic acids, as shown in Fig. 139, or to mixtures of different reacting materials. Sometimes the point of inflection in the curve is not sufficiently pronounced to determine accurately and then it is helpful to plot tangents of the curve, $\Delta E/\Delta V$, against the volume V of reagent added as shown in Fig. 141. The sharp peak in this curve gives the end-point with certainty. The second graph may be obtained by drawing tangents at points of the first curve or it may be obtained directly from the original data by dividing the differences in electromotive force by the corresponding differences in cubic centimeters.

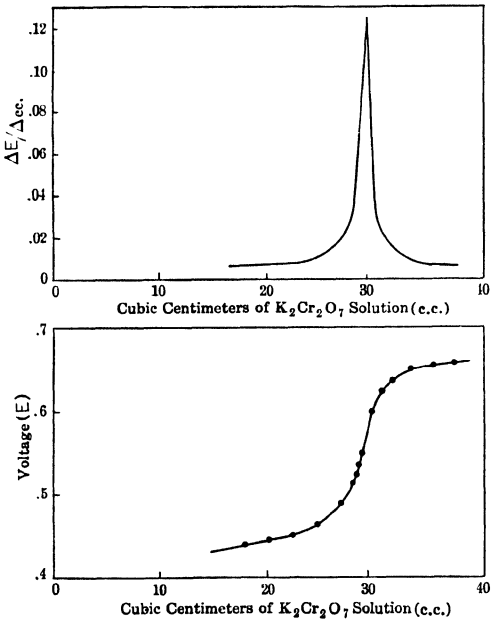


FIG. 141

Potentiometric titrations do not demand the greatest accuracy in voltage measurements, and a simple voltmeter-potentiometer similar to that shown in Fig. 137 is usually satisfactory. An ordinary platinum wire is simply immersed in the solution for oxidation-reduction titrations. It constitutes one electrode and the calomel reference-electrode is the other electrode.

In addition to neutralizations and oxidations it is possible to obtain end-points in the case of precipitations. The titration of iodide with silver nitrate is a simple example. A silver wire is placed in the solu-

tion and connected to a calomel reference-electrode through a galvanometer which is set at zero by balancing against it an equal potential from a battery and adjustable rheostat. As the silver solution is added, the galvanometer remains near zero because the silver ion concentration is fixed by the solubility of silver iodide. When all the iodide is precipitated, however, the next drop increases the silver ion concentration enormously and the galvanometer is deflected sharply. A different end-point is obtained for bromides and the two may be titrated together in the same solution.

Bimetallic electrodes can sometimes be used in a very simple way. The calomel electrode is unnecessary, and two electrodes, one of platinum and the other of platinum-rhodium, are immersed in the solution. The potential of the platinum-rhodium electrode does not change appreciably whereas the potential of the platinum wire responds to changes in the concentration of oxidizing and reducing ions or hydrogen and hydroxyl ions. Near the end-point, when the two opposing ions are equal, a sudden, large change in voltage is produced by a small amount of reagent. Various bimetallic combinations may be used, such as platinum-tungsten, platinum-"Carborundum," platinum-gold, tungsten-copper, etc.* A similar result may be achieved by using two electrodes of the same metal and polarizing one by electrolysis.

Differential titration is capable of great accuracy. A small part of the original solution is isolated around one of the two electrodes (platinum wires) and, as the titration proceeds, the greatest difference in potential between the two electrodes for a given addition of titrant is registered at the end-point,† for then the ratio of the two different concentrations is greatest.

The Debye-Hückel Theory. The interionic attraction theory has already been employed to explain in a qualitative way various phenomena involving ions. It was shown on p. 199 that the mutual attraction between positive and negative ions at ordinary concentrations leads to a smaller decrease in vapor pressure than is to be expected on the assumption of complete separation at infinite dilution. This effect leads also to similar decreases in the freezing-point depression and the other colligative properties. Abnormalities in solubilities

* Hostetter and Roberts, J. Am. Chem. Soc., **41**, 1337 (1919); Willard and Fenwick, J. Am. Chem. Soc., **44**, 2504, 2516 (1922); Kahlenberg, Trans. Am. Electrochem. Soc. **56**, 201 (1929).

† MacInnes and Dole, J. Am. Chem. Soc., **51**, 1119 (1929); Hall, Jensen and Bäckström, J. Am. Chem. Soc., **50**, 2217 (1928); Müller, Z. physik. Chem., **135**, 102 (1928).

and solubility products and single electrode potentials were interpreted also on the basis of this theory (p. 410). The change in electrical conductances of strong electrolytes with concentration was also explained by the theory (p. 381).

The idea of complete dissociation of strong electrolytes and the interionic attraction theory have been incorporated into the quantitative theory of Debye and Hückel.* This theory has been remarkably successful when applied to dilute solutions.

The mathematical development of the Debye-Hückel equation is beyond the scope of this book, but it may be stated that it is based on the work required to separate the ions in the process of dilution. The attractive or repulsive forces are governed by Coulomb's law of charged bodies and depend on the magnitude of the ionic charges and the distance between ions as given by the expression e_1e_2/Dr^2 where e_1 and e_2 represent the charges, D the dielectric constant of the solvent, and r the average distance between them. In very dilute solutions r becomes so great that this attractive force approaches zero and the simple laws of complete dissociation are adequate. Debye and Hückel calculated that, under the conditions of mutual attraction, the distance r between ions is inversely proportional to the square root of the concentration and were led to the following formula:

$$1 - g = w\frac{e^2}{6\,k\,DT}\sqrt{\frac{4\,\pi e^2}{k\,DT}}n\nu \qquad (86)$$

where

e = unit charge of ion = 4.77×10^{-10} electrostatic units.
D = dielectric constant of the solution = 88.2 for water at 273° K.
k = gas constant per molecule = $R/N = 1.372 \times 10^{-16}$ erg.
n = ions per cc. = $6.06 \times 10^{20}\,c$, where c = molar concentration.
ν = number of ions formed by the dissociating molecule, 2, 3, etc.
w = a valence factor $\left(\frac{\sum \nu z^2}{\sum \nu}\right)^{\frac{3}{2}}$, which is the summation for each ion of the product of its number times the square of its valence, z; divided by the total number of ions; and raised to the 3/2 power.

g = osmotic coefficient defined on p. 201; the ratio of the observed osmotic pressure to the idealized osmotic pressure under conditions of complete dissociation into ν ions, assuming no interionic attraction.

* Milner, Phil. Mag., **35**, 214 (1918); Debye and Hückel, Physik. Z., **24**, 185, 305 (1923); Debye, Physik. Z., **25**, 97, (1924); Hückel, Ergebnisse exakt. Wissenschaften, III, 199 (1924); Noyes, J. Am. Chem. Soc., **46**, 1080, 1098 (1924); **47**, 2122 (1925).

The factor w bears a close resemblance to the ionic strength, μ, defined on p. 200. Making the proper substitutions for numerical values, equation (86) becomes

$$1 - g = 0.38\, z_1 z_2 \sqrt{\mu} \qquad (87)$$

for a salt, composed of two different kinds of ions, dissolved in water at 25°.

One of the best tests of this equation depends on an important relation* that $-\ln \gamma = 3(1 - g)$ where γ is the activity coefficient of the electrolyte. Then equation (87) becomes

$$-\log \gamma = 3/2.3(1 - g) = 0.5\, z_1 z_2 \sqrt{\mu} \qquad (88)$$

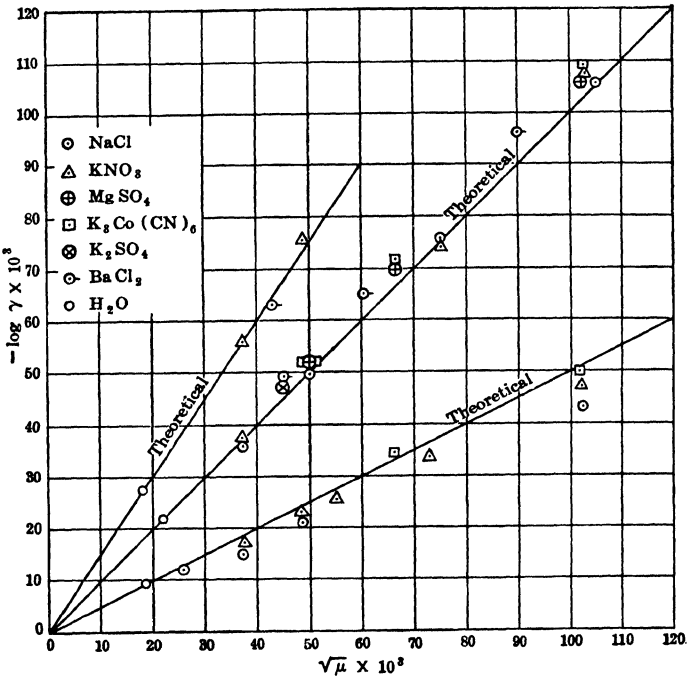


FIG. 142

A test of this equation is shown in Fig. 142. Brönsted and La Mer† determined the solubility of certain complex cobaltammines in salt solutions of various valence types and compared the solubility with the solubility in pure water, thus obtaining values of the activity coefficients, γ. In Fig. 142, $-\log \gamma$ is plotted against $\sqrt{\mu}$ and the

* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 346. Brönsted and La Mer, J. Am. Chem. Soc. **46**, 559 (1924).

† J. Am. Chem. Soc. **46**, 555 (1924).

lowest line corresponds to a uni-univalent cobalt compound where z_1z_2 is 1, and the slope is seen to be 0.5. The ionic strength of the solution rather than the specific nature of the added salt determines the value of γ. The next line corresponds to a cobalt salt of the uni-bivalent type where z_1z_2 has a value of 2, and the slope is $2 \times 0.5 = 1$. The steepest line in Fig. 142 corresponds to a uni-trivalent compound where z_1z_2 is 3, and the slope is 1.5. This equation gives a theoretical justification for the ionic strength μ which Lewis found, empirically, to be of considerable importance in the study of electrolytes. It emphasizes the fact that *in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.*

A similar equation has been applied also to irreversible processes, such as the electrical conductance and viscosity of dilute solutions of strong electrolytes.

It has been determined, experimentally, that the time of relaxation of the ionic atmosphere is of particular significance in the problem of the electrical conductance of solutions. The results of the theoretical calculations may be given by means of an equation of the form

$$\Lambda = \Lambda_\infty - \Lambda_{\mathrm{I}} - \Lambda_{\mathrm{II}} \tag{89}$$

where Λ_∞ is the equivalent conductance at infinite dilution, Λ_{I} is a measure of the electrical force of relaxation, and Λ_{II} measures the electrophoretic force which is due to the fact that the ions are hydrated and moving toward opposite electrodes in a moving rather than a stationary solvent. Both forces resist the migration of the ions and it can be shown that they are proportional to the square root of the concentration, c. Equation (89) may then be written as follows:

$$\Lambda = \Lambda_\infty - A\sqrt{c}, \tag{90}$$

where A is a constant which depends among other things upon the dielectric constant of the medium, the absolute temperature, and the mobilites of the ions.*

This equation was discovered empirically by Kohlrausch during the first investigations of electrolytes and it was indicated graphically in Fig. 122 on p. 377.

The viscosity of strong electrolytes has been treated in a similar manner by Falkenhagen and Dole.†

* Complete details are given by Williams and Falkenhagen, Chem. Rev., **6**, 317 (1929).

† Physik. Z., **30**, 611 (1929); Z. physik. Chem., **B 6**, 159 (1929).

REFERENCES

Treatise on Physical Chemistry, Chapters XII and XIII. Taylor.
Thermodynamics and Free Energy of Chemical Substances, Chapters XXII, XXIII, XXV, XXVI, XXVII, XXIX, XXX. Lewis and Randall.
Thermodynamics and Chemistry, Chapter XVII. Macdougall.
Potentiometric Titrations. Kolthoff. (Translated by Furman.)
Determination of Hydrogen Ions, Chapters VIII to XVIII. Clark.
Colorimetric and Potentiometric Determination of *p*H. Kolthoff.
Applied Electrochemistry, Chapter VIII. Allmand.
Grundzüge der Elektrochemie. Grübe.

PROBLEMS*

1. The temperature coefficient of the cell

$$\text{Pb, } PbCl_2, \text{ KCl } (0.1\ m), \text{ HgCl, Hg}$$

is 0.0002 volt per degree and its electromotive force at 25° is 0.535 volt. (*a*) What is the heat of the cell reaction,

$$\text{Pb } (s) + 2\ \text{HgCl } (s) \rightarrow PbCl_2\ (s) + 2\ \text{Hg } (l)$$

at 25°? (*b*) What is the free energy change? *Ans.* (*a*) $-\Delta H = 21{,}925$ cal.

2. The electromotive force of the cell

$$\text{Pb, } PbSO_4, Na_2SO_4 \cdot 10\ H_2O \text{ (sat.)}, Hg_2SO_4, \text{Hg}$$

is 0.9647 volt at 25°. The temperature coefficient is 0.000174 volt per degree. Calculate (*a*) the heat of the reaction and (*b*) the free energy change of the reaction.

$$\text{Pb } (s) + Hg_2SO_4\ (s) \rightarrow PbSO_4\ (s) + 2\ \text{Hg } (l).$$

3. The potential of the cell

$$\text{Zn, } ZnCl_2 \text{ (sp. gr. 1.391)}, \text{HgCl, Hg}$$

is 1.0000 volt at 15° and 1.00047 volts at 20°. What is the average heat of the reaction

$$\text{Zn } (s) + 2\ \text{HgCl } (s) \rightarrow ZnCl_2 \text{ (sp. gr. 1.391)} + 2\ \text{Hg } (l)$$

between 15° and 20°?

4. Using the values of normal electrode potentials given on page 442, (*a*) calculate the normal potential of each of the following cells and (*b*) state which is the negative electrode in each cell:

(1) $\text{Zn, } Zn^{++}(a = 1) \parallel Ag^{+}(a = 1), \text{Ag}$
(2) $\text{Ag, } Ag^{+}(a = 1) \parallel Cu^{++}(a = 1), \text{Cu}$
(3) $\text{Zn, } Zn^{++}(a = 1) \parallel (Cl^{-}(a = 1), Cl_2)\text{Pt}$
(4) $\text{Pb, } Pb^{++}(a = 1) \parallel Sn^{++}(a = 1), \text{Sn}$
(5) $\text{Pt}(Br_2, Br^{-}(a = 1)) \parallel (Cl^{-}(a = 1), Cl_2)\text{Pt}$

Ans. (1). (*a*) 1.5596. (*b*) Zn negative.
(2). (*a*) −0.4537. (*b*) Cu negative.

* In these problems | indicates the presence of a liquid junction potential and ‖ indicates that the liquid junction potential has been eliminated. The concentrations *m* are grams per 1000 grams of H_2O (molal concentrations).

The normal calomel electrode has the potential 0.281.

5. (*a*) Calculate the potential, (*b*) write the reaction, and (*c*) calculate the free energy change for each of the following cells:

(1) Li, $Li^+(a = 1) \parallel (Cl^-(a = 1), Cl_2(g\ 1\ atm.))Pt$
(2) Pb, $Pb^{++}(a = 1) \parallel Ag^+(a = 1)$, Ag
(3) Cu, $Cu^{++}(a = 1) \parallel Na^+(a = 1)$, Na
(4) Cd, $Cd^{++}(a = 1) \parallel (I^-(a = 1), I_2\ (s))Pt$

Ans. (1). (*a*) $E = 4.3178$ volts. (*b*) $Li\ (s) + \frac{1}{2}\ Cl_2(g\ 1\ atm.) \rightarrow Li^+(a = 1) + Cl^-(a = 1)$. (*c*) $\Delta F = -99{,}570$ cal.

6. (*a*) Calculate the potentials of the following cells:

(1) $Pt(Fe^{+++}(a = 1), Fe^{++}(a = 1)) \parallel (Tl^{+++}(a = 1), Tl^+(a = 1))Pt$
(2) $Pt(Sn^{++++}(a = 1), Sn^{++}(a = 1)) \parallel (Hg^{++}(a = 1), Hg^+(a = 1))Pt$
(3) $Pt(Ti^{++++}(a = 1), Ti^{+++}(a = 1)) \parallel (Ce^{++++}(a = 1), Ce^{+++}(a = 1))Pt$

(*b*) Write the reaction for each cell and (*c*) state which reactions go spontaneously in the direction written.

Ans. (1). (*a*) 0.4633 volt. (*b*) $2\ Fe^{++}(a = 1) + Tl^{+++}(a = 1) \rightarrow 2\ Fe^{+++}(a = 1) + Tl^+(a = 1)$. (*c*) Reaction as written is spontaneous.

7. (*a*) Construct a cell in which the reaction is

$$\frac{1}{2}\ Cl_2\ (g\ 1\ atm.) + Br^-(a = 1) \rightarrow Cl^-(a = 1) + \frac{1}{2}\ Br_2\ (l)$$

(*b*) Determine the potential from values given in the table of normal electrode potentials and (*c*) calculate the free energy of the reaction.

Ans. (*a*) $(Pt)Br_2\ (l), Br^-(a = 1) \parallel Cl^-(a = 1), Cl_2\ (g\ 1\ atm.)(Pt)$. (*b*) 0.2935 volt. (*c*) $\Delta F = -6770$.

8. (*a*) Construct a cell in which the reaction is

$$\frac{1}{2}\ Cu\ (s) + \frac{1}{2}\ Cl_2\ (g.\ 1\ atm.) \rightarrow \frac{1}{2}\ Cu^{++}(a = 1) + Cl^-(a = 1)$$

(*b*) What is the potential of the cell and (*c*) the free energy of the reaction? (*d*) What difference would there be in the solution of this problem if the reaction were written

$$Cu\ (s) + Cl_2\ (g\ 1\ atm.) \rightarrow Cu^{++}(a = 1) + 2\ Cl^-(a = 1)?$$

Ans. (*b*) 1.0142. (*c*) $\Delta F = -23{,}388$.

9. Write the reaction of the cell

$$Pt(Fe^{+++}(a = 1), Fe^{++}(a = 1)) \parallel Ag^+(a = 1), Ag$$

Calculate (*a*) the cell potential and (*b*) the free energy of the reaction at 25°. (*c*) What is the value of the equilibrium constant? (*d*) What would be the activity of Ag^+ ions in equilibrium with solid silver in a solution containing Fe^{+++} and Fe^{++} at unit activity?

Ans. (*a*) $E = 0.0501$. (*b*) $\Delta F = -1155$ cal. (*c*) $K = 7.031$. (*d*) $a_{Ag^+} = 0.142$.

10. Write the reaction of the cell

$$Pt(Fe^{+++}(a = 2), Fe^{++}(a = 0.1)) \parallel Ag^+(a = 1), Ag$$

Calculate (*a*) the cell potential and (*b*) the free energy of the reaction at 25°. (*c*) Compare the results with those of the preceding problem. How would you account for the differences?

Ans. (*a*) −0.0269 volt.

11. The electromotive force of the cell

$$\mathrm{Pt(H_2(1\ atm.),\ H^+(}a = 1\mathrm{))} \parallel \mathrm{(Ce(NO_3)_4(0.0164}\ m\mathrm{),\ Ce(NO_3)_3(0.0584}\ m\mathrm{))Pt}$$

is 1.52 volts at 25°. On the assumption that the activities of the ceric and cerous ions are proportional to the concentrations of the corresponding nitrates, calculate the normal potential of the ceric-cerous ion electrode. *Ans.* 1.5526 volts.

12. The electromotive force of the cell

$$\text{Normal calomel electrode} \parallel \begin{pmatrix} \mathrm{FeCl_3}\ (0.1\ m) \\ \mathrm{FeCl_2}\ (0.1\ m) \\ \mathrm{HCl}\ (0.1\ m) \end{pmatrix} \mathrm{Pt}$$

is 0.446 volt at 25°. The hydrochloric acid is added to prevent hydrolysis. Assuming that the activity coefficients of the Fe^{+++} and Fe^{++} ions are 0.75 and 0.87 respectively, calculate the value of E^0 for the ferric-ferrous electrode containing 0.1 *m* HCl.

13. Ceric salts are sometimes used as oxidizing agents in quantitative analysis. Calculate the equilibrium constant of the following reaction

$$Ce^{++++} + Fe^{++} \rightarrow Fe^{+++} + Ce^{+++}$$

at 25° from electromotive force data. In the titration of a ferrous salt with a ceric salt at 25°, (*a*) what fraction of the iron would still be in the ferrous state at the stoichiometric point? Assume that $a_{Fe^{+++}} = a_{Ce^{+++}}$ and $a_{Fe^{++}} = a_{Ce^{++++}}$ at that point. (*b*) Follow in a qualitative way the changes in the activity of each of the four ions involved in such a titration.

Ans. (*a*) 1.65×10^{-7}.

14. The electromotive force of the cell

$$\text{Normal calomel electrode} \parallel \mathrm{Pb(NO_3)_2(0.01}\ m\mathrm{)},\ \mathrm{Pb}$$

is −0.467 volt at 25°. Assuming that the activity coefficient of the Pb^{++} ion in 0.01 *m* lead nitrate is 0.69, calculate the value of E^0 for the Pb^{++}, Pb electrode.

15. Calculate the potentials of the following cells at 25°. $E^0_{Ni^{++},Ni} = -0.231$ volt.

(*a*) Ni, Ni^{++} ($a = 0.001$) ‖ Pb^{++} ($a = 0.05$), Pb

(*b*) Pt(Sn^{++++} ($a = 0.8$), Sn^{++} ($a = 0.001$)) ‖ (Fe^{+++} ($a = 0.002$), Fe^{++} ($a = 0.5$))Pt

Ans. (*a*) 0.159.

16. Some of the older literature contains values of normal electrode potentials on the basis of the normal calomel electrode having an absolute potential of 0.56 volt. A value of 0.426 volt was given to the stannic-stannous electrode. What potential would this represent on the basis of the normal hydrogen electrode having zero potential?

17. Calculate the potentials of the following cells at 25°.

(*a*) Zn, Zn^{++} ($a = 0.0005$) ‖ Cd^{++} ($a = 0.2$), Cd

(*b*) Pt(Cr^{+++} ($a = 0.4$), Cr^{++} ($a = 0.02$)) ‖ (Co^{+++} ($a = 0.001$), Co^{++} ($a = 0.8$))Pt

18. What is the electromotive force of the cell

$$\text{Cu amalgam (I), solution } \mathrm{CuSO_4}\text{, Cu amalgam (II)}$$

having given that the activities of the copper in the amalgams (I) and (II) are 0.0147 and 0.0466 respectively? *Ans.* −0.0148.

19. Calculate the potential of the cell

$$\text{Cu, } CuSO_4 \text{ (0.01 } m\text{) } \| \text{ } CuSO_4 \text{ (1 } m\text{), Cu}$$

at 25°, having given the following values for the activity coefficients of the Cu^{++} ion in the two solutions; for 1 m copper sulphate $\gamma = 0.16$, and for 0.01 m copper sulphate $\gamma = 0.4$. *Ans.* 0.0473.

20. At 25° the electromotive force of the cell

$$\text{Zn, } ZnSO_4 \text{ (0.05 } m\text{) } \| \text{ } ZnSO_4 \text{ (0.005 } m\text{), Zn}$$

is −0.0217 volt. Assuming the activity coefficient of the Zn ion to be 0.59 in the dilute solution, what is the activity coefficient in the more concentrated solution?

21. What is the potential of the cell

$$\text{Zn, } ZnSO_4 \text{ (0.01 } m\text{) } | \text{ } ZnSO_4 \text{ (0.1 } m\text{), Zn}$$

at 25°? For $ZnSO_4$, $n_a = \frac{v}{u+v} = 0.6$, and the activity coefficients of the Zn^{++} ion are 0.23 in 0.1 m $ZnSO_4$ and 0.5 in 0.01 m $ZnSO_4$.

22. The electromotive force of the cell

$$\text{Hg, } HgCl, \text{ NaCl (0.01 } m\text{) } \| \text{ normal calomel electrode}$$

is −0.1207 volt and that of the cell

$$\text{Hg, } HgCl, \text{ NaCl (0.001 } m\text{) } \| \text{ normal calomel electrode}$$

is −0.1780 volt, the temperature being 25°. Assume that the activity coefficients of the Cl^- ion in these solutions are equal to the mean activity coefficients of the NaCl. Obtain the activity coefficient of the 0.001 m NaCl from the table on p. 451 and calculate that of the 0.01 m solution. *Ans.* 0.903.

23. The cell

$$\text{K(amalgam), KCl (0.01 } m\text{), AgCl, Ag, AgCl, KCl (0.1 } m\text{), K(amalgam)}$$

is reversible to both cation and anion. Calculate its potential, using the activity coefficients given in the table. *Ans.* 0.110.

24. At 25° the potential of the cell

$$\text{Ag, AgI, KI (1 } m\text{) } \| \text{ } AgNO_3 \text{ (0.001 } m\text{), Ag}$$

is 0.72 volt. In a molal solution of KI the activity coefficient of I^- ion is 0.65 and in 0.001 m $AgNO_3$ the activity coefficient of Ag^+ ion is 0.98. (*a*) What is the solubility product of AgI? (*b*) Assuming no salt effect, what would be the solubility of AgI in pure water? *Ans.* (*b*) 2.1×10^{-8} mols per 1000 g. H_2O.

25. What are the potentials of the following half cells at 25°?

(*a*) $Pt(H_2$ (1 atm.), $H^+(a = 1))$
(*b*) $Pt(H_2$ (2 atm.), $H^+(a = 1))$
(*c*) $Pt(H_2$ (1 atm.), $H^+(a = 0.1))$
(*d*) $Pt(H_2$ (2 atm.), $H^+(a = 0.1))$
(*e*) $(H^+(a = 0.1), H_2$ (1 atm.))Pt

Ans. (*b*) 0.0089. (*c*) +0.0591.

26. What are the potentials of the following cells?

(*a*) $Pt(H_2$ (0.1 atm.), $H^+(a = 1))$ ‖ normal hydrogen electrode
(*b*) Normal hydrogen electrode ‖ $(H^+(a = 0.0001), H_2$ (1 atm.))Pt

(*c*) Normal calomel electrode || ($H^+(a = 0.0001)$, H_2 (1 atm.))Pt

(*d*) Pt(H_2 (1 atm.), $H^+(a = 0.0001)$) || normal calomel electrode

(*e*) Normal calomel electrode || ($H^+(a = 0.0004)$, H_2 (1 atm.))Pt

27. Express the following hydrogen ion activities as *p*H values: (*a*) 0.01, (*b*) 0.0002, (*c*) 10^{-8}, (*d*) 1.5, and (*e*) $4 \cdot 10^{-13}$.

Ans. (*a*) 2. (*b*) 3.7. (*d*) −0.18.

28. Express the following *p*H values as H^+ ion activities. (*a*) 4.7, (*b*) 12, (*c*) 8.06, (*d*) 1.4, and (*e*) −0.3. *Ans.* (*a*) 2×10^{-5} (*d*) 4×10^{-2}.

29. Assuming that the H^+ ion activity coefficient is equal to the mean activity coefficient of the solute and that $K_w = 10^{-14}$, calculate the *p*H of the following solutions: (*a*) 0.001 *m* HCl, (*b*) 1 *m* HCl, (*c*) 4 *m* HCl, (*d*) 0.1 *m* KOH. The activity coefficients of hydrochloric acid and potassium hydroxide are given in the tables.

30. What is the potential developed by a cell composed of a normal calomel electrode and a hydrogen electrode (1 atm.) immersed in a solution (*a*) of *p*H 6.0? (*b*) of *p*H 10.0? *Ans.* (*a*) 0.635.

31. (*a*) A potential of 0.514 volt was obtained at 25° for a solution when placed in the cell

Pt(H_2 (1 atm.), (solution)) || normal calomel electrode

What is the *p*H of the solution?

(*b*) Under similar conditions with another solution a potential of 0.829 was obtained. What is the *p*H of this solution? *Ans.* (*a*) 3.95.

32. The cell

Normal calomel electrode || (solution, quinhydrone)Pt

was found to have a potential of 0.179 volt for a certain solution at 25°. What is the *p*H of the solution? *Ans.* 4.05.

33. The electromotive force of the cell

Pt(H_2 (1 atm.), $C_6H_5NH_2 \cdot HCl$ (0.03125 *m*)) || normal calomel electrode

is 0.464 volt at 25°. Calculate the degree of hydrolysis of the aniline hydrochloride. *Ans.* 2.5 per cent.

34. Calculate the electromotive force of the cell

Hg, HgCl, KCl (0.01 *m*) || normal calomel electrode

at 25° from these data:

Hg, HgCl, KCl (0.1 *m*) || normal calomel electrode. $E_{298} = -0.0529$
Activity of Cl^- in 0.01 *m* KCl at 25° = 0.00899
Activity of Cl^- in 0.1 *m* KCl at 25° = 0.0764

35. The cell

Pt(H_2 (1 atm.), KOH (0.01 *m*)) | (KCl (0.01 *m*), HgCl, Hg

has a potential of 1.0820 volts at 25°. At this temperature the equivalent conductances of 0.01 *m* KOH and 0.01 *m* KCl are 255.8 and 141.2 respectively. Determine the potential of the above cell corrected for the junction potential. Using the value of the potential of the cell

Hg, HgCl, KCl (0.01 *m*) || normal calomel electrode

at 25° as −0.1079 volt, find the potential of the cell

Pt(H_2 (1 atm.), KOH (0.01 *m*)) || normal calomel electrode

36. The activity coefficient of OH^- in 0.01 *m* KOH is 0.901 at 25° and the potential of the cell

$$Pt(H_2\ (1\ atm.),\ KOH\ (0.01\ m))\ \|\ \text{normal calomel electrode}$$

is +0.9894 volt at this temperature. What is the ionic product ($K_w = a_{H^+} \times a_{OH^-}$) of water at 25°?

Ans. $K_w = 0.93 \times 10^{-14}$.

CHAPTER XVIII

ELECTROLYSIS AND POLARIZATION

Galvanic and Electrolytic Cells. The preceding chapter has been devoted to a consideration of galvanic or voltaic cells; cells in which chemical energy is transformed into electrical energy. We shall now consider very briefly the behavior of *electrolytic cells*, or cells in which electrical energy is consumed in effecting the decomposition of electrolytes. While the processes occurring within most of the galvanic cells treated in the preceding chapter are largely reversible, the processes occurring within electrolytic cells are almost wholly irreversible.

Current Density and Current Concentration. Two important factors involved in electrolytic processes are *current density* and *current concentration*. The ratio of the current strength in amperes to the area of the electrodes of an electrolytic cell, expressed in square decimeters, is known as the current density. The terms "cathodic" and "anodic" current density are employed to express the intensity of current per unit of area of the cathode or anode surface, respectively, in an electrolytic cell. The ratio of the current strength to the number of cubic centimeters of electrolyte is termed the "current concentration."

Current Efficiency. While theoretically 96,500 coulombs of electricity is required to separate one gram-equivalent of a substance in electrolysis, practically it is found that a greater quantity of electricity is required. This fact, however, does not imply a failure of Faraday's laws but rather is to be attributed to a number of causes among which may be mentioned the following: (1) current leakage; (2) secondary reactions; and (3) loss of products of electrolysis. The ratio of the theoretical quantity of electricity to that actually required to effect the separation of a known weight of substance is termed the *current efficiency*. Current efficiency is a factor of great importance in all electrolytic processes.

Energy Efficiency. If it were possible to conduct an electrolytic process in a perfectly reversible manner and with a current efficiency of 100 per cent, the quantity of electrical energy required would be equal to the product of the quantity of electricity used and the so-called "theoretical decomposition voltage." The actual, or working voltage, however, is always greater than the theoretical voltage, owing to

the fact that the electrode processes are not strictly reversible and also because of the resistance of the electrolyte. The ratio of the theoretical quantity of electrical energy to the quantity actually employed is known as the *energy efficiency*. The energy efficiency, like the current efficiency, of an electrolytic process is a factor of outstanding importance in all technical calculations involving electrolytic cells.

Polarization. If a difference of potential of about 1 volt is applied to two platinum electrodes, immersed in a concentrated solution of hydrochloric acid, it will be found that the current which passes at first will steadily diminish and ultimately will become zero. The cessation of the current is due to the accumulation of hydrogen on the cathode and chlorine on the anode, these two gases setting up an opposing electromotive force, called the *electromotive force of polarization*. If the applied electromotive force is increased to 1.5 volts, the counter-electromotive force will no longer be sufficient to reduce the current to zero. In fact, at any voltage above 1.35 volts, a continuous current passes at atmospheric pressure. This is termed the *decomposition potential* of hydrochloric acid.

At all voltages above the decomposition potential, the current, C, may be calculated by means of the formula,

$$E - e = CR, \tag{1}$$

where E is the applied electromotive force, e the counter-electromotive force, and R the resistance of the electrolyte. As the applied electromotive force and the current increase, the polarization increases, since the gases are liberated under a pressure greater than that of the atmosphere. Since, however, the gases escape from the solution, the value of e can never become equal to E.

The decomposition potential of an electrolyte can be determined in either of two different ways: (1) by gradually raising the applied electromotive force, E, until it exceeds e, when the current will suddenly increase; or (2) by charging the electrodes up to atmospheric pressure by means of an electromotive force greater than e, and after breaking the external circuit, measuring the counter-electromotive force.

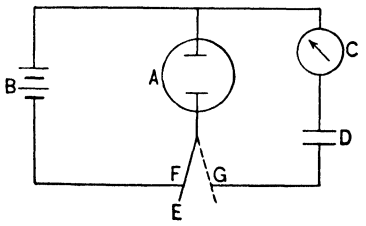


FIG. 143

The arrangement of apparatus for the measurement of the electromotive force of polarization, as suggested by Le Blanc,* is indicated in Fig. 143; A is the electrolytic cell in

* Z. phsyik. Chem., **5**, 469 (1890).

which polarization occurs, B is the source of external electromotive force, C is a capillary electrometer, D is a source of variable potential, and E is one prong of an electrically driven tuning-fork which serves to make and break contact in rapid alternation with the points, F and G. When the tuning-fork makes contact at F, the current flows through A, polarizing the electrodes; when contact is made at G, the counter-electromotive force, due to polarization, causes a current to flow through D and C. The counter-electromotive force is balanced by varying D, until no current flows through C. The potential of D is then equal to the electromotive force of polarization.

Polarization may be due to a chemical or physical change on the surface of the electrode, or to the deposition of a film of gas or oxide or other material, or it may be due only to a change in concentration of the electrolyte in the neighborhood of the electrode.

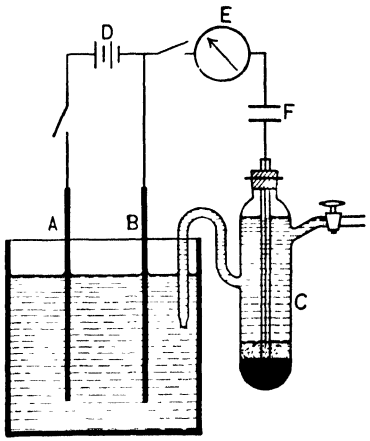


FIG. 144

The method employed for the measurement of polarization at a single electrode was devised by Fuchs, and is illustrated diagrammatically in Fig. 144. The two electrodes, A and B, and the side tube of the normal calomel electrode, C, are immersed in the vessel containing the electrolyte; D is the source of external electromotive force, E is an electrometer, and F is a source of variable potential. Before the external circuit, DAB, is closed, the potential of the electrode, B, against the solution is measured. Then the circuit, DAB, is closed, thereby polarizing the electrode B. The external circuit is now broken, and the potential of B against the solution remeasured. The difference between the final and initial values of the electrode potential gives the value of the polarization at B. In like manner, the polarization at the other electrode can be measured.

The small amount of electricity which is necessary to polarize an electrode is termed the *polarization capacity of the electrode.* This factor is dependent upon the extent of surface of the electrode, and also upon the nature of the metal of which it is formed. The polarization capacity of palladium is greater than that of platinum, for electrodes of equal surface, when hydrogen is liberated on each. Palladium dissolves hydrogen more readily than does platinum, and consequently a

larger amount of hydrogen, and a correspondingly greater quantity of electricity will be required to bring the hydrogen dissolved in the palladium up to the same pressure as that of the hydrogen dissolved in the platinum. If, through the processes of solution or diffusion, or through chemical action, the substance which causes the polarization is removed, the electrode is said to be *depolarized*. Thus, when a reducing agent, such as ferrous chloride, is electrolyzed, the oxygen liberated at the anode immediately combines with the electrolyte, forming ferric chloride, and polarization of the electrode is prevented.

If water is electrolyzed between platinum electrodes, the cathode becomes saturated with hydrogen, and the anode with oxygen, until, when the electromotive force of polarization becomes equal to that of the external circuit, the current ceases. The two gases, hydrogen and oxygen, are soluble, however, and consequently diffuse away from the electrodes, either escaping from the solution, or recombining to form water. In order to compensate for this continuous loss of gas at the electrodes, a small current continues to flow, thus maintaining the initial electromotive force constant. This small current is termed the *residual current*. If oxygen is bubbled over the surface of the cathode during electrolysis, the hydrogen is removed as rapidly as it is liberated. Such an electrode, on which no new substance is formed during electrolysis, is called an *unpolarizable electrode*.

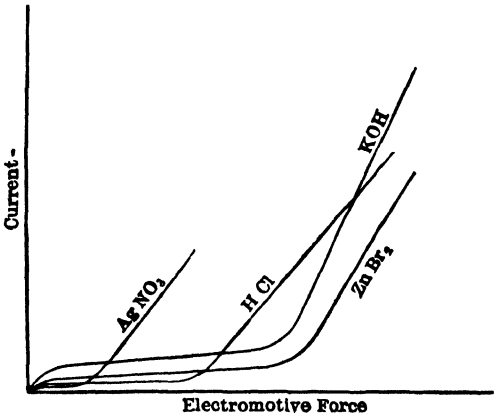


FIG. 145

Decomposition Potentials. The decomposition potential of an electrolyte can be determined, as has already been pointed out, by immersing two platinum electrodes in the solution and connecting with a source of electricity, the electromotive force of which can be varied at will. The voltage is gradually increased and the corresponding current is observed. It is found that the current increases at first, and then drops almost to zero every time the voltage is raised, until the decomposition potential is ultimately reached. Beyond this point the current has been found to be directly proportional to the electromotive force. If the applied electromotive forces are plotted as abscissas, and the corresponding currents as ordinates,

we obtain curves of the form shown in Fig. 145. Some of the decomposition potentials of molar solutions, as determined by Le Blanc,* are given in the accompanying tables.

DECOMPOSITION POTENTIALS

SALTS

Salt	Decomp. Potential	Salt	Decomp. Potential
	Volts		Volts
$ZnSO_4$	2.35	$Cd(NO_3)_2$	1.98
$ZnBr_2$	1.80	$CdSO_4$	2.03
$NiSO_4$	2.09	$CdCl_2$	1.88
$NiCl_2$	1.85	$CoSO_4$	1.92
$Pb(NO_3)_2$	1.52	$CoCl_2$	1.78
$AgNO_3$	0.70		

ACIDS

Acid	Decomp. Potential
	Volts
H_2SO_4	1.67
HNO_3	1.69
H_3PO_4	1.70
$CH_2Cl.COOH$	1.72
$CHCl_2.COOH$	1.66
$CH_2(COOH)_2$	1.69
$HClO_4$	1.65
HCl	1.31
$(COOH)_2$	0.95
HBr	0.94
HI	0.52

BASES

Base	Decomp. Potential
	Volts
$NaOH$	1.69
KOH	1.67
NH_4OH	1.74

* Z. physik. Chem., 8, 299 (1891).

It will be observed that, although there is considerable variation in the decomposition potentials of salts, there is very little variation in the decomposition potentials of acids and bases. There is a maximum value of about 1.70 volts to which many acids and bases closely approximate. It is found that all acids and bases which decompose at 1.70 volts give off hydrogen and oxygen at the electrodes. Those acids and bases which decompose at potentials less than the maximum do not liberate hydrogen and oxygen. When their solutions are sufficiently diluted, however, hydrogen and oxygen are evolved, and the decomposition potential rises to the maximum value. Thus, Le Blanc found the following values for the decomposition potential of different solutions of hydrochloric acid, using polished platinum electrodes.

DECOMPOSITION POTENTIALS OF HCl

Concentration	Decomp. Potential
	Volts
2 *m* HCl	1.26
$\frac{1}{2}$ *m* HCl	1.34
$\frac{1}{6}$ *m* HCl	1.41
$\frac{1}{16}$ *m* HCl	1 62
$\frac{1}{32}$ *m* HCl	1.69

The anode is surrounded by hydroxyl ions and by chloride ions which are discharged when the electrons are removed. The hydroxyl ion loses its electron more easily than does the chloride ion, as indicated by the positions in the electromotive force series, and when the two ions are present in equal amounts practically pure oxygen is produced. However, when the concentration of the chloride ions is much greater than that of the hydroxyl ions, chlorine is produced by the removal of electrons from the chloride ions. When 2 *m* hydrochloric acid is electrolyzed, hydrogen and chlorine are evolved, but when the concentration of the solution is reduced to $m/32$, hydrogen and oxygen are evolved, and the usual decomposition potential of 1.70 volts is obtained.

When the products of electrolysis are gaseous, the value of the decomposition potential depends upon the nature of the electrodes. Thus, under certain conditions, the cell,

$$Pt_{H_2} - m\ H_2SO_4 - Pt_{O_2}$$

gives an electromotive force of 1.07 volts, if platinized platinum electrodes are used. If an external electromotive force slightly greater

than 1.07 volts is applied to this cell, in the reverse direction, a continuous decomposition of water will take place, and hydrogen and oxygen will be evolved at the electrodes. If, on the other hand, the platinized electrodes are replaced by electrodes of polished platinum, the decomposition potential will be found to rise to 1.67 volts. The reverse electromotive force of polarization, however, is found to be only 1.07 volts. That is, the liberation of gas at a polished platinum electrode is an irreversible process. The difference in the behavior of the two electrodes is explicable when it is remembered that platinum is capable of occluding large amounts of gas. A platinized electrode absorbs the liberated gas very slowly, and when thoroughly saturated, if it is not entirely immersed in the solution, it gradually gives up the gas by diffusion, no bubbles being formed. Thus, if the external electromotive force is raised to 1.07 volt, the system will be in equilibrium; if the applied electromotive force is greater, or less, than the equilibrium value, a current will flow in one direction, or the other, gas being either liberated or dissolved.

Where polished platinum or gold electrodes are used, however, the decomposition potential is 1.67 volts. Polished electrodes have relatively small absorbing power. Hence, if an electromotive force between 1.07 and 1.67 volts is applied, the gases cannot diffuse away from the electrode rapidly enough, and, when the solution in the vicinity of the electrodes becomes saturated with gas, the current will cease flowing. A very slow process of diffusion from the solution into the air is constantly taking place, however, and this permits the continuous evolution of an exceedingly small amount of gas, while a correspondingly small current traverses the solution.

In order to produce a steady electrolysis, it is necessary to raise the external electromotive force to such an intensity that bubbles are formed continuously at the surface of the electrodes. This calls for the performance of work, the amount of which is dependent upon the condition of the electrode surfaces, the surface tension of the solution, and various other factors. In cases where bubbles are formed, a portion of the available energy of the chemical process is not expended in effecting electrical separation; consequently, the reverse electromotive force is less than the applied, and the system is irreversible.

Passivity. It has long been known that if a piece of iron is momentarily immersed in concentrated nitric acid and then thoroughly rinsed in water, it not only becomes insoluble in acid but also fails to precipitate copper from solutions of its salts. This peculiar phenomenon is known as *passivity*, and the metal is said to be in the *passive state*. Other metals, such as chromium and nickel, also exhibit the

phenomenon of passivity. Many metals acquire the property of passivity on being made the anode in an electrolytic cell. When in the passive state, the metals resemble the so-called "noble metals" in their behavior, and if they dissolve at all when functioning as the anode in a cell, the amount entering the solution is found not to correspond with that required by Faraday's law. For example, both chromium and manganese, when in the passive state, exhibit in solution a higher valence than when in the ordinary, or active state. Normally, chromium should dissolve as the Cr^{++} ion, but when it is made the anode in an alkaline electrolyte, it does not dissolve until the potential attains a value of approximately $+0.34$ volt. It then enters the solution as hexavalent Cr^{6+} ions, which immediately react with the hydroxyl ions to form chromate ions according to the reaction,

$$Cr^{6+} + 8\ OH^- = CrO_4^{--} + 4\ H_2O.$$

As a general rule, however, as the anodic current-density is increased, the proportion of the current carried by the ions of the metal entering the solution diminishes, the anions are discharged, and ultimately the metal ceases to dissolve. Under these conditions the function of the current is merely to discharge the anions. The higher the current-density, the greater the passivity becomes. It is evident, therefore, that an intimate connection exists between passivity and polarization.

The subject of passivity has engaged the attention of chemists for many years, and numerous ingenious theories have been advanced in explanation of the phenomenon. These theories have been compiled and critically reviewed by Byers* and also by Bennett and Burnham,† who conclude that passivity is probably due to the formation of a film of adsorbed oxide which acts as a protective layer.

Overvoltage. The reactions occurring at the electrode of an electrolytic cell are catalytically accelerated by the metal of which the electrodes are formed. Thus, platinized platinum is the most effective catalyst for the reaction represented by the equation,

$$H_2 \rightleftarrows 2\ H^+ + 2\ e.$$

When hydrogen is liberated on polished platinum 0.29 volt more is required than when it is liberated on platinized platinum, and when it is liberated on zinc, 1.06 volts more is required. The electromotive force necessary to overcome the resistance of the chemical reaction at an electrode is termed *overvoltage*. Thus, we say that hydrogen is liberated on polished platinum with an overvoltage of 0.29 volt, and on

* Byers, J. Am. Chem. Soc., **30**, 1718 (1908).

† Bennett and Burnham, Trans. Am. Electrochem. Soc., **29**, 217 (1916).

zinc with an overvoltage of 1.06 volts. The following table gives the overvoltage of hydrogen and oxygen, i.e. the difference between the observed potential and the potential under reversible conditions. The overvoltages change greatly with current density and cannot be measured accurately.

ELECTRODE OVERVOLTAGES

Current density = 0.1 amp. per cm.^{2} Temp. = 25°. I.C.T. VI, 339.

Hydrogen Liberation		Oxygen Liberation	
Cathode	Overvoltage	Anode	Overvoltage
Pt (platinized)	0.00	Pt (polished)	1.28
Pt (polished)	0.29	Au	1.24
Au	0.59	Ag	0.98
Fe	0.82	Ni (polished)	0.726
Ag	0.87	Ni (spongy)	0.687
Ni	1.05	Cu	0.66
Zn	1.06	Pt (platinized)	0.64
Pb	1.18		
Sn	1.22		

Various theories as to the cause of overvoltage have been advanced, but the phenomenon has not been fully explained.*

MacInnes and Adler,† as a result of their experimental studies on hydrogen overvoltage, conclude that it is due primarily to a layer of supersaturated, dissolved hydrogen in the electrolyte surrounding an electrode. If the electrode is capable of adsorbing sufficient hydrogen to form nuclei for bubbles of gas, the supersaturation cannot rise to high values, and the electrode will have a low overvoltage. On the other hand, metals possessing small adsorptive powers exhibit high overvoltages.

Electrolytic Separation of the Metals. Freudenberg‡ was the first to recognize the possibility of effecting the quantitative separation of different metals by means of graded electromotive forces. He showed that it is only necessary to select salts of each metal, whose respective decomposition potentials differ as widely as possible, and electrolyze at an electromotive force intermediate between these potentials. The salt having the lower decomposition potential will decompose first, and when the deposition of the metal is complete, the current will practically cease flowing; then if the applied electromotive force

* Newbery, J. Am. Chem. Soc., **105**, 2419 (1914).

† J. Am. Chem. Soc., **41**, 194 (1919).

‡ Z. physik. Chem., **12**, 97 (1893).

is raised above the decomposition potential of the second salt, the second metal will be deposited. In practice it is found necessary to increase the applied electromotive force slightly, because of the gradual decrease in the number of ions of the salt having the lower decomposition potential. For example, suppose a mixture of the nitrates of cadmium, lead and silver is subjected to electrolysis, the decomposition potentials of the salts being as follows:— $Cd(NO_3)_2$ = 1.98 volts, $Pb(NO_3)_2$ = 1.52 volts, and $AgNO_3$ = 0.70 volt. If the applied electromotive force is made a little less than 1 volt all of the silver will be deposited; then if the electromotive force is raised to about 1.6 volts, all of the lead will be deposited; and finally, if the electromotive force is raised to about 2 volts the cadmium will be deposited.

In the subjoined table are given the separation potentials of some of the ions, the separation potential of the H^+ ion being assumed to be equal to zero.

SEPARATION VALUES OF IONS FOR MOLAR CONCENTRATION

Ion	Separation Potential	Ion	Separation Potential
Ag^+	+0.78	I^-	+0 52
Cu^{++}	+0.34	Br^-	+0.94
H^+	0.0	O^{--}	+1.08 (in acid)
Pb^{++}	−0.17	Cl^-	+1.31
Cd^{++}	−0.38	OH^-	+1.68 (in acid)
Zn^{++}	−0.74	OH^-	+0.88 (in base)
		SO_4^{--}	+1.9

According to this table the decomposition potential of water is equal to the sum of the separation potentials of its ions, or 1.68 volts.

If a solution of potassium sulphate is electrolyzed, hydrogen and oxygen are evolved because the hydrogen and hydroxyl ions are discharged at a lower voltage than the potassium ions and sulphate ions, as indicated by the normal electrode potentials. However, with very large current densities it is possible to deplete the hydrogen ions in the immediate neighborhood of the cathode to such an extent that some potassium will then deposit in a mercury cathode.

The control of concentration as well as voltage is important in practical electroplating. In nickel plating, for example, if the acidity of the plating baths exceeds a certain limit, hydrogen will be liberated and the deposit will not be firm and smooth. The electroplating of a mixture of copper and zinc (brass) is another example. Ordinarily,

copper is plated exclusively, when a mixture of zinc and copper salts is electrolyzed, because its decomposition potential is much less. However, the concentration of copper ions can be decreased enormously by adding potassium cyanide and locking up most of the copper in complex ions; under these conditions, when the zinc is very concentrated, both metals will be deposited together at the cathode.

Storage Cells. Storage cells or accumulators, as the name implies, are devices for the storage of electrical energy in the form of chemical energy. Any reversible cell may be employed as a storage cell. Practically, however, only two types of such secondary cells are in use to-day. These are the almost universally used lead storage cell, and the less efficient nickel-iron storage cell.

If two lead plates are immersed in a 20 per cent solution of sulphuric acid, a minute amount of lead sulphate will be formed on the surface of each plate. If now a current of electricity is passed through the solution, the lead sulphate on the cathode will undergo reduction to metallic lead, and the lead sulphate on the anode will be oxidized to lead peroxide. In this manner we form the cell,

$$Pb, PbSO_4, H_2SO_4\ (20\%), PbSO_4, PbO_2, Pb.$$

The electromotive force of this cell is about 2 volts. The amounts of lead and lead peroxide produced in this way are so small that the cell has only a very small capacity. In order to increase its capacity, the electrodes should be given as large an amount of surface as possible. This may be brought about by the method of Planté, in which a solution of sulphuric acid is electrolyzed, first in one direction and then in the other, thus causing the plates to become spongy; or by the method of Faure, in which a lead "grid" charged with a paste of lead oxide and red lead is introduced into a similar solution, and a current passed until spongy lead is formed at the cathode and lead peroxide is formed at the anode. If the charging circuit is then broken and the two electrodes are connected by a wire, electrons will flow through the wire from the lead plate to the peroxide plate, while lead sulphate is slowly formed at each.

According to Le Blanc the following reactions take place during the discharge of the lead storage cell:

Negative Electrode.

(a) $Pb \rightarrow Pb^{++} + 2\,e.$

(b) $Pb^{++} + SO_4^{--} \rightarrow PbSO_4$ (solid).

Hence the total reaction at the negative electrode is

$$Pb + SO_4^{--} \rightarrow PbSO_4 + 2\,e.$$

Positive Electrode.

(a) PbO_2 (solid) $\rightarrow Pb^{++++} + 2\,O^{--}$.

(b) $4\,H^+ + 2\,O^{--} \rightarrow 2\,H_2O$.

(c) $Pb^{++++} + 2\,e \rightarrow Pb^{++}$.

(d) $Pb^{++} + SO_4^{--} \rightarrow PbSO_4$ (solid).

The total reaction at the positive electrode is, therefore,

$$PbO_2 + 4\,H^+ + SO_4^{--} + 2\,e \rightarrow PbSO_4 + 2\,H_2O.$$

On combining the two preceding equations, we have, as the equation for the reaction of the cell as a whole,

$$PbO_2 + Pb + 2\,H_2SO_4 \rightarrow 2\,PbSO_4 + 2\,H_2O.$$

Since, on charging the cell, the foregoing reactions take place in the reverse direction, it follows that the reactions corresponding to both processes may be represented by a single equation, thus

$$PbO_2 + Pb + 2\,H_2SO_4 \underset{\text{(charge)}}{\overset{\text{(discharge)}}{\rightleftarrows}} 2\,PbSO_4 + 2\,H_2O.$$

This equation represents the reactions of the lead storage cell according to the double sulphate theory, i.e., the theory based on the formation of lead sulphate at both electrodes during discharge.

Vosburgh and Craig* have calculated the normal potential of the cell by a study of the cells

$$Hg,\ Hg_2SO_4,\ PbSO_4,\ H_2SO_4 \,||\, H_2SO_4,\ PbSO_4,\ PbO_2,\ Pt$$

and

$$Pb,\ PbSO_4,\ SO_4^{--} \,||\, SO_4^{--},\ PbSO_4,\ Hg_2SO_4,\ Hg.$$

Their value, 2.03 volts, should be the potential of a lead storage cell containing sulphuric acid at unit activity. Calculations of the potential for various concentrations of acid were in such good agreement with previously determined values that they may be considered as proof of the double sulphate theory.

A typical pair of charge and discharge curves for the lead accumulator are shown in Fig. 146. The ampere-hour efficiency of the lead cell is approximately 95 per cent; the watt-hour, or energy efficiency, which is dependent upon the rate of charge and discharge, ranges from 75 to 85 per cent.

Since lead storage cells have come into such general use, it may not be amiss to include in this section a few directions as to their care and maintenance.

It is important that a storage cell should never be discharged below

* J. Am. Chem. Soc. **51**, 2009 (1929).

1.80 volts. Cells should never be permitted to remain discharged, but as soon as the voltage drops to 1.80 volts they should be immediately recharged. When allowed to stand in a discharged condition for any length of time, "sulphating" occurs, i.e., hard crystals of lead sulphate are formed on the plates, thereby rendering subsequent attempts to recharge the cell exceedingly difficult. In charging, care must be taken to employ only direct current, and to connect the positive wire with the positive terminal of the cell. The rate at which cells should be charged is also of importance, and is generally designated on the cell by the manufacturer. Cells should be charged until the voltage becomes constant and free evolution of gás has continued for at least two hours. During this period, no further increase in specific gravity of the electrolyte, as indicated by a hydrometer, should be noted. The value of the specific gravity of the electrolyte of a fully charged storage cell is 1.210 to 1.215. Fresh electrolyte should never be added to a cell until it has been determined that the proper specific gravity cannot be secured by charging alone. Sufficient distilled water should be added from time to time to insure the complete immersion of the electrodes in the solution because the effective surface is reduced if the plates dry out. Care should be taken to remove any sediment which may collect in the battery jars before it comes in contact with the bottom of the electrodes.

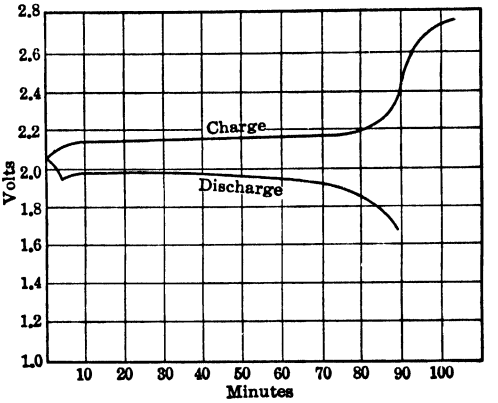


FIG. 146

There is no danger of freezing a fully charged battery, but when a battery is allowed to become discharged or nearly discharged the concentration of sulphuric acid is not sufficiently great to prevent freezing at temperatures only a few degrees below 0° C. The expansion on freezing may cause serious mechanical injury.

The Nickel Oxide Storage Cell. This secondary cell, invented by Edison and sometimes called the "Edison Battery," consists of two electrodes, one of nickelic oxide and the other of pure iron, immersed in a solution of potassium hydroxide, as indicated by the scheme,

Fe, KOH, Ni_2O_3.

The reactions on charging and discharging the nickel oxide accumulator may be summarized by the equation

$$Fe + 2\ Ni(OH)_3 \underset{(charge)}{\overset{(discharge)}{\rightleftarrows}} 2\ Ni(OH)_2 + Fe(OH)_2.$$

The electrolyte is found to undergo no change during the operation of the cell. The initial normal electromotive force of the nickel oxide cell is 1.35 volts. Its ampere-hour efficiency is relatively low, amounting to approximately 82 per cent; its watt-hour efficiency is only 59 per cent.

Storage batteries are used so extensively that any new improvements would be important, particularly in developing intermittent sources of power, such as windmills and tide motors.

Depolarization and Electrolysis. As has previously been stated, an agent which is capable of lessening, or entirely eliminating, polarization is known as a depolarizer. Depolarizers can function in either of two ways. They may act as catalysts in accelerating the process which is responsible for the depolarization, or they may act by reducing the energy consumption at the electrode to a value below that which corresponds to the equilibrium electrode potential. As an illustration of the first mode of action, the liberation of hydrogen at a cathode surface may be cited. While the polarization is often very great at the surface of ordinary metallic cathodes, it may be practically eliminated by the substitution of a platinized platinum electrode. The second mode of action of a depolarizer may be illustrated by the Bunsen primary cell, in which the anode is of zinc and the cathode of platinum or carbon, while both electrodes are surrounded by concentrated nitric acid. When weak acid only is used, the cathode reaction consists in the discharge of hydrogen ions, with a resultant electromotive force of about 0.7 volt. With concentrated acid, however, the cathode reaction is depolarized; hydrogen ions are no longer discharged but are oxidized to form water and the resultant electromotive force rises to approximately 1.0 volt. In other words, depolarization, in this case, consists in altering the former electrode process and substituting for it a reaction which takes place with the consumption of less energy. Depolarization may also be effected in some cases by purely mechanical means, such as vigorous stirring.

Both cathodic and anodic depolarizers are known. A cathodic depolarizer is a substance which readily undergoes reduction, whereas an anodic depolarizer is a substance which can be easily oxidized. Numerous organic compounds are capable of functioning as depolarizers, due to the fact that many of them react with the products formed by the

discharge of the ions. As a rule, the reactions involved in anodic depolarization are much more varied than those occurring in cathodic depolarization.

Electrolytic Reduction. By varying the conditions of electrolysis, it is possible to obtain with the same depolarizer an entire series of different reduction products. For example, Haber* has shown that by the electrolytic reduction of nitrobenzene, $C_6H_5NO_2$, in both acid and alkaline solution under different experimental conditions, it is possible to obtain the following series of reduction products:

Nitrosobenzene	C_6H_5NO,
β-Phenylhydroxylamine	$C_6H_5 \cdot NH \cdot OH$,
Azoxybenzene	$C_6H_5 \cdot N(\rightarrow O) - N \cdot C_6H_5$,
Azobenzene	$C_6H_5 \cdot N = N \cdot C_6H_5$,
Hydrazobenzene	$C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$,
Aniline	$C_6H_5 \cdot NH_2$.

This illustrates in a striking manner the superiority of electrochemical reduction methods to ordinary chemical methods in which a different reducing agent is required for each reduction product, and where contamination by the reducing agent is almost certain to occur. In the foregoing series of reduction products of nitrobenzene, excellent yields of at least four of the substances — aniline, azoxybenzene, azobenzene and hydrazobenzene — can be obtained by the electrolytic method by suitable control of temperature, cathode potential and the acidity or alkalinity of the solution.

Of the various factors affecting the efficiency of electrolytic reduction, the cathode potential is the most important. This quantity may be calculated by means of the equation,

$$E = -\frac{RT}{F} \ln \frac{k \cdot c_H}{c_{H^+}}, \qquad (2)$$

where c_H is the concentration of the nascent hydrogen in the electrode, c_{H^+} the concentration of the hydrogen ions in the solution and k a constant. Since c_{H^+} may be assumed to remain practically constant, it follows that the cathode potential will vary directly with the concentration of the active hydrogen, and, therefore, according to the law of mass action, the reducing power of the cathode will be proportional to its potential.

* Haber, Z. Elektrochem., **4**, 506 (1898); Z. physik. Chem., **32**, 193 (1900).

Another important factor in electrolytic reduction is the velocity of depolarization. The electrolytic reduction of a depolarizer is often a two-fold process which may be represented by the reactions,

(a) $H^+ + e \rightarrow H$,

and (b) Depolarizer + H → Reduction product.

It is apparent that, if the first reaction has a higher velocity than the second, the concentration of the active, atomic hydrogen will increase and a corresponding increase in the cathode potential will occur. When the cathode potential reaches a certain value, molecular hydrogen will be liberated at the electrode. The curves obtained by plotting cathode potentials against corresponding values of current strength afford an illustration of the foregoing statements. In Fig. 147, *ABCD* represents the curve of hydrogen evolution from an electrolyte containing no depolarizer, while *ABE* is the curve obtained with the same solution to which has been added a depolarizer which reacts rapidly with nascent hydrogen. It is important to note that the higher the velocity of depolarization, the more efficient is the reduction. Since the cathode potential increases with the current-density, it may happen, if too high current-densities are employed, that the potential current curve will intersect the curve of hydrogen evolution, as in the case of the curve *ABF* in Fig. 147. Since the point *G*, at which these two curves intersect, corresponds to the cathode potential necessary for the liberation of gaseous hydrogen, it follows that a portion of the current will be consumed in producing gaseous hydrogen at the expense of a greater reduction of the depolarizer. Not only is the cathode potential increased by high current-density, but also the concentration of the depolarizer in the immediate vicinity of the cathode is lowered. It follows, therefore, that low current-densities tend to increase the efficiency of processes involving electrolytic reduction.

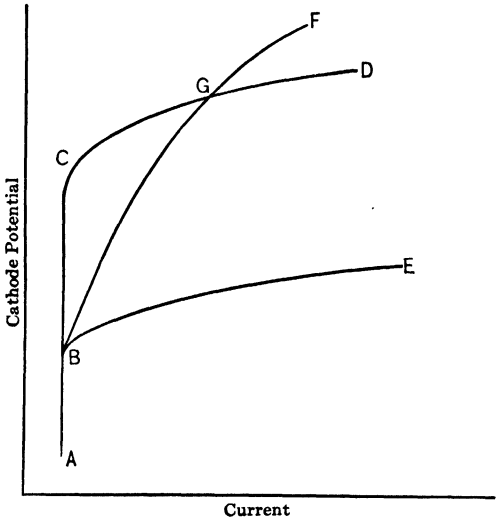


FIG. 147

There yet remains another factor which exercises a marked influence on the efficiency of electrolytic reduction processes. This third factor is the presence of catalysts in the electrolyte. It has been found that the presence of a small amount of an appropriate catalyst very appreciably accelerates the reaction between a depolarizer and the nascent hydrogen liberated at the cathode of an electrolytic cell. For example, the yield of hydroquinone obtained by the electrolytic reduction of an acid solution of quinone at a platinum cathode is greatly increased by the addition to the electrolyte of a minute quantity of titanic chloride. The latter is rapidly reduced at the cathode to the titanous salt, and this in turn reduces the quinone to hydroquinone. The titanous salt, however, is oxidized in the process and the same cycle can thus be repeated indefinitely.

The cathode itself may also function as a catalyst. Cathodes of different metals have been found to accelerate the reaction between a given depolarizer and hydrogen at very different rates. As a consequence of this fact, the same reduction process can take place at a much lower cathode potential with some cathodes than with others. It follows, therefore, that at the same cathode potential, the permissible current-density can be widely varied. The influence of the nature of the cathode upon the current-potential curve is clearly shown in Fig. 148, where the results of a series of experiments with different electrodes employed in the reduction of an alkaline solution of potassium nitrate are represented graphically.

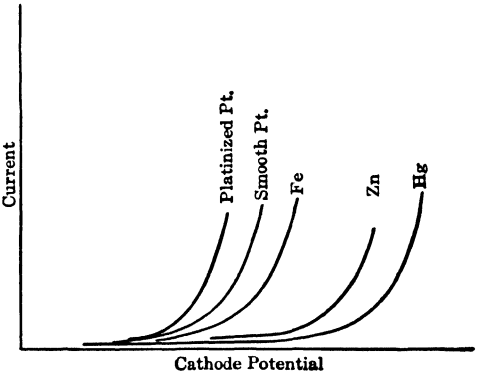


FIG. 148

Electrolytic Oxidation. The principal anodic process involved in electrolytic oxidation processes is represented by the equation,

$$2\,OH^- \rightarrow H_2O + \tfrac{1}{2}\,O_2 + 2\,e.$$

This process is invariably accompanied by irreversible effects which render accurate measurements of the electrode potential impossible. In general it may be stated that the process of electrolytic oxidation closely resembles the process of electrolytic reduction, and the same generalizations which have been stated as applying to the one apply also to the other. In electrolytic oxidation processes, however, only

a limited number of metals can be employed as anodes, since it is important that the electrodes should be attacked as little as possible by the products of electrolysis. The metals which fulfil this requirement most satisfactorily are platinum, iridium, palladium and iron, for processes occurring in alkaline solutions, but the platinum metals alone seem to be best adapted to electrolysis in acid solutions.

In carrying out electrolytic oxidations it is of the utmost importance that reduction of the products of oxidation at the cathode be prevented. This may be accomplished by the use of a porous diaphragm and a relatively small cathode surface which possesses a low hydrogen overvoltage. Cathodic reduction may also be prevented by adding to the electrolyte a small amount of potassium chromate. This causes the formation of a thin film of insoluble chromium chromate around the cathode and thus prevents the oxidation product from coming in direct contact with it.

REFERENCES

Electrochemistry. Creighton and Fink.
Applied Electrochemistry, Chapters IX and X. Allmand.
Applied Electrochemistry. Thompson.
Electrochemistry of Organic Compounds. Löb. (Translated by H. W. F. Lorenz.)
Organic Electrochemistry. Brockman.
Electrolytic Preparations. Elbs. (Translated by R. S. Hutton.)
Storage Batteries. Vinal.

PROBLEMS

1. What must the concentration of Cu^{++} ions be in order that the deposition potential of copper from solution will be the same as the deposition potential of zinc from a solution containing Zn^{++} ions at unit activity?

2. An electrolytic cell containing a cadmium sulphate solution was subjected to various applied potentials and the corresponding currents were measured. The results were shown as follows:

E (volts)	0.5	1.0	1.5	1.8	2.0	2.2	2.4	2.6	3.0
I (amperes)	0.002	0.004	0.006	0.007	0.008	0.028	0.069	0.110	0.192

What is the decomposition potential of cadmium sulphate? *Ans.* 2.06 volts.

3. A solution at 25° contains Ni^{++} ions at an activity of 0.1. If the solution is too acid hydrogen will be deposited on the cathode instead of nickel. What should the pH of the solution be so that the hydrogen will not be liberated until the potential is 0.1 volt greater than the potential required to deposit the nickel? The overvoltage of hydrogen on nickel may be assumed to be 0.2 volt. $E^0_{Ni^{++}, Ni} = -0.231$ volt.

4. Explain why the overvoltage of hydrogen on lead is a factor in the successful use of the lead storage cell.

5. The common, Le Clanche dry cell consists of an electrode of graphite and manganese dioxide, immersed in a saturated solution of ammonium chloride (to-

gether with zinc chloride and starch) and sealed into a zinc container which acts as the other electrode. The chief reaction of the cell is

$$Zn + 2\,NH_4^+ = Zn^{++} + 2\,NH_4 = Zn^{++} + 2\,NH_3 + 2\,H$$

(*a*) Explain why the zinc is not rapidly attacked by the ammonium ions when the cell stands idle on open circuit.

(*b*) Explain why the cell would be rapidly polarized and give but a small output of electricity, in the absence of the manganese dioxide.

CHAPTER XIX

CHEMICAL THERMODYNAMICS*

Calculation of Free Energy. The important relations between equilibrium constants, free energy changes, and electromotive force of galvanic cells have been discussed in earlier chapters. In this chapter the further application of thermodynamical principles to chemical calculations will be described briefly, using the notation of Lewis and Randall as described in their "Thermodynamics and the Free Energy of Chemical Substances."

If the free energy change in a chemical reaction cannot be determined directly from equilibrium measurements or from electrode potentials, it can still be calculated indirectly from other reactions. If several reactions are added together, the equilibrium constants are not additive, but the free energy changes are additive just as heats of reaction are additive. The free energy change of the total reaction is the sum of the free energy changes of all the composite reactions.

The addition of free energy equations may be illustrated by the calculation of the free energy of formation of hydrochloric acid from its elements at 25° C., ΔF as usual being expressed in calories.

(a)		$H_2O(l) = H_2O(g)$.	$\Delta F = 2{,}053.$
(b)		$H_2(g) + \frac{1}{2} O_2(g) = H_2O(l)$.	$\Delta F = -56{,}560.$
(c)	= (a + b)	$H_2(g) + \frac{1}{2} O_2(g) = H_2O(g)$.	$\Delta F = -54{,}507.$
(d)		$H_2O(g) + Cl_2(g) = 2\,HCl(g) + \frac{1}{2} O_2(g)$.	$\Delta F = 9{,}120.$
(e)	= (c + d)	$H_2(g) + Cl_2(g) = 2\,HCl(g)$.	$\Delta F = -45{,}387.$
(f)		$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) = HCl(g)$.	$\Delta F = -22{,}693.$

Just as we have tables of heats of formation (p. 251) from which we can calculate heats of reaction, so also we have tables of free energy of formation from which we can calculate ΔF for various reactions. The free energy of formation of the elements at 25° and atmospheric pressure, in their natural states under these conditions, are taken as zero. A table giving a few of these values follows.

* This chapter, particularly in the sections on activities, is quite technical, and of necessity it is abbreviated. It may be omitted without affecting the chapters which follow.

TABLE OF FREE ENERGIES OF FORMATION AT 25° C.

Substance	ΔF^0_{298}	Substance	ΔF^0_{298}
$H_2(g)$	0	$NH_3(g)$	− 3,910
$H_2O(l)$	−56,560	$NO(g)$	20,869
$H_2O(g)$	−54,507	$NO_2(g)$	12,495
$Cl_2(g)$	0	$CO(g)$	−32,510
$HCl(g)$	−22,692	$CO_2(g)$	−94,260
$HBr(g)$	−12,540	$HCOOH(aq)$	−87,920
$HI(g)$	315	$CO(NH_2)_2(s)$	−47,280
S(rhombic)	0	$PbO(s)$	−45,050
S(monoclinic)	18	Ag^+	18,448
$S(g)$	30,240	Zn^{++}	−34,984
$H_2S(g)$	− 7,840		

To illustrate the use of this table in calculating free energy changes, we may take the reaction

$$\tfrac{1}{2}\ Cl_2 + HBr = \tfrac{1}{2}\ Br_2 + HCl.$$

$$\Delta F^0 = \Delta F^0_{\text{products}} - \Delta F^0_{\text{reactants}} = [0 + (-22{,}692)] - [0 + (-12{,}540)] = -10{,}152.$$

The calculation of free energies from equilibrium constants; and equilibrium constants from free energies, is very simple as given by the following equation derived on p. 273.

$$\Delta F^0 = -RT \ln K, \tag{1}$$

both ΔF and R being usually expressed in calories. The equation may be illustrated with the dissociation constant of nitrogen tetroxide at 25°. For the reaction $N_2O_4 \rightleftarrows 2\ NO_2$,

$$K = \frac{p^2_{NO_2}}{p_{N_2O_4}} = 0.1426,$$

and

$$\Delta F^0 = -RT \ln K = -1.987 \times 298 \times 2.303 \log 0.1426 = +1154 \text{ cal.}$$

This relation means that, in order to dissociate one mol of N_2O_4 at unit activity into two mols of NO_2 at unit activity, free energy amounting to 1154 calories must be supplied.

It is essential to have a clear understanding of the influence of concentration in changing the value and even the sign of ΔF^0. For example, in a simple hypothetical reaction

$$A \rightleftarrows B$$

if the system is at equilibrium when A and B are at equal activities,

$$K = \frac{a_B}{a_A} = \frac{1}{1} \quad \text{and} \quad \Delta F^0 = -RT \ln K = -RT \ln 1 = 0.$$

If the system is in a state of equilibrium at 27° when the activity or effective concentration of B is ten times as great as that of A,

$$K = \frac{a_B}{a_A} = \frac{10}{1}, \text{ and } \Delta F^0 = -RT \ln K = -2 \times 300 \times 2.3 \log 10$$
$$= -1380 \text{ cal.}$$

Always, there is a tendency for the reactants (the materials at the left of the reaction as written) at unit activity to react to give the products at unit activity if ΔF^0 has a negative sign, i.e., if the free energy of the products is less than the free energy of the reactants.

If the system is in a state of equilibrium when the activities of the products are less than those of the reactants, ΔF^0 is positive; there is no tendency for the reactants at unit activity to react to give the products at unit activity, but on the contrary the reaction tends to go in the reverse direction. If the activity of the products is one-tenth of the activity of the reactant at equilibrium at 27°,

$$K = \frac{a_B}{a_A} = \frac{1}{10}, \text{ and } \Delta F^0 = -RT \ln K = -2 \times 300 \times 2.3 \log \frac{1}{10}$$
$$= -2 \times 300 \times 2.3 \times (-1) = +1380.$$

Influence of Temperature on Free Energy Change. It is often necessary to calculate the free energy change of a chemical reaction at one temperature from data obtained at another temperature. Such a calculation may be made with the help of the Gibbs-Helmholtz equation and a knowledge of the heat of reaction and the heat capacities. This equation, derived on p. 133, may be written

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

Differentiating $\frac{\Delta F}{T}$ with respect to temperature at constant pressure

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = -\Delta H T^{-2} + \frac{1}{T}\frac{\partial(\Delta H)}{\partial T} + \frac{\partial\left(\frac{\partial \Delta F}{\partial T}\right)}{\partial T}.$$

It can be shown by a theorem involving entropy that the last term is equal to $-\frac{\Delta C_p}{T}$, and the next to the last term is seen to be equal to $\frac{\Delta C_p}{T}$.

Therefore the last two terms cancel and

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = -\frac{\Delta H}{T^2}. \tag{3}$$

But ΔH depends on the temperature and on the difference between the heat capacity of the products and the reactants (p. 258), according to the equation

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_p \, dT \tag{4}$$

where ΔH_0 is a constant, a hypothetical heat of reaction at absolute zero assuming that the relations determined experimentally at ordinary temperatures hold down to the absolute zero. Since the heat capacity of a substance can usually be expressed by a parabolic equation of the type

$$C_p = \Gamma_0 + \Gamma_1 T + \Gamma_2 T^2 + \cdots \tag{5}$$

and since the difference between the heat capacity of the reactants and the products is

$$\Delta C_p = C_{p\,(\text{products})} - C_{p\,(\text{reactants})} = \Delta\Gamma_0 + \Delta\Gamma_1 T + \Delta\Gamma_2 T^2 + \cdots \tag{6}$$

we have on substituting into equation (4) and integrating,

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_p \, dT = \Delta H_0 + \Delta\Gamma_0 T + \tfrac{1}{2}\Delta\Gamma_1 T^2 + \tfrac{1}{3}\Delta\Gamma_2 T^3 + \cdots \tag{7}$$

and again substituting equation (7) into equation (3)

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = \frac{-\Delta H}{T^2} = \frac{-\Delta H_0 - \Delta\Gamma_0 T - \frac{1}{2}\Delta\Gamma_1 T^2 - \frac{1}{3}\Delta\Gamma_2 T^3}{T^2}. \tag{8}$$

On integrating

$$\frac{\Delta F}{T} = \frac{\Delta H_0}{T} - \Delta\Gamma_0 \ln T - \tfrac{1}{2}\Delta\Gamma_1 T - \tfrac{1}{6}\Delta\Gamma_2 T^2 \cdots + I, \tag{9}$$

and

$$\Delta F = \Delta H_0 - \Delta\Gamma_0 T \ln T - \tfrac{1}{2}\Delta\Gamma_1 T^2 - \tfrac{1}{6}\Delta\Gamma_2 T^3 \cdots + IT. \tag{10}$$

The integration constant ΔH_0 must be evaluated by the experimental determination of ΔH at some temperature; and the integration constant I must be evaluated by the experimental determination of ΔF at some one definite temperature. The use of this equation may be

illustrated in the calculation of the free energy of formation of hydrochloric acid, as follows:

$$\tfrac{1}{2}\,H_2 + \tfrac{1}{2}\,Cl_2 = HCl, \qquad \Delta F_{298} = -22{,}692, \qquad \Delta H_{291} = -22{,}000.$$

By equation (4) $$\Delta H_0 = \Delta H - \int_0^T \Delta C_p\, dT.$$

$$\Delta C_p = C_{p,HCl} - (\tfrac{1}{2}\,C_{p,H_2} + \tfrac{1}{2}\,C_{p,Cl_2}) = 6.5 + 0.001\,T - \left(\frac{6.5 + 0.0009\,T}{2} + \frac{7.4 + 0.001\,T}{2}\right) = -0.45 + 0.00005\,T$$

(p. 255).

$$\Delta H_0 = -22{,}000 + 0.45 \times 291 - \tfrac{1}{2} \times 0.00005 \times 291^2 = -22{,}000 + 131 - 2 = -21{,}871.$$

Substituting in equation (10)

$$-22{,}692 = -21{,}871 + 0.45 \times 298 \times 2.303 \times 2.474 - \tfrac{1}{2} \times 0.00005 \times 298^2 + 298\,I,$$

$$I = \frac{-22{,}692 + 21{,}871 - 764 + 2}{298} = -5.31$$

and $$\Delta F^0 = -21{,}871 + 0.45\,T \ln T - 0.000025\,T^2 - 5.31\,T.$$

Activities. Activities have been discussed on pp. 273, 448, and it has been emphasized that the mass law and the laws of thermodynamics may be applied with exactness when activities a are used.

Formulas involving activities were derived, but when these formulas were applied to practical problems concentrations were often substituted for activities. The results were only approximately correct except in very dilute solutions where the activities and the concentrations are essentially equal. In some cases activity coefficients were arbitrarily given, so that concentrations could be converted into activities. It is the purpose of this section to show how activities may be determined experimentally.

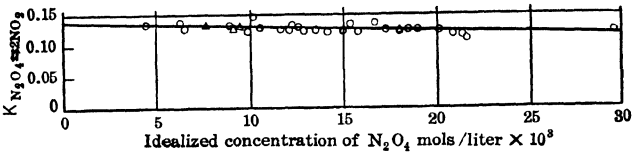


FIG. 149

A good illustration of the need of activities in thermodynamical calculations is shown in the determination of the dissociation constant at 25° C. of N_2O_4, at different total concentrations,* as shown in Fig. 149. If N_2O_4 and NO_2 behaved as perfect gases, the law of concentration

* Verhoek and Daniels, J. Am. Chem. Soc., **53**, 1250 (1931).

effect should hold exactly and the values of the dissociation constant, calculated from $K = \frac{p^2_{NO_2}}{p_{N_2O_4}}$, should be independent of the concentration of material, and when K is plotted against the total concentration of material, a horizontal line should be produced. It is evident from Fig. 149, however, that K increases 13 per cent as the total pressure is reduced from one atmosphere to one-tenth of an atmosphere. In the derivation of the relation, $\Delta F^0 = -RT \ln K$, it is assumed that the gases are ideal gases, and accordingly the correct value to use in thermodynamical calculations is the value extrapolated to zero pressure where the gases are strictly ideal. In this case K has a value of 0.1426 at zero pressure. Sometimes it is possible in this way to obtain a correct equilibrium constant or a normal electrode potential by extrapolation to infinite dilution without direct determination of the activities. More often it is necessary to obtain the activities by reference to some standard state.

At a definite temperature a pure, volatile liquid has a definite tendency to pass off into the vapor state; this tendency is measured by its vapor pressure. If a second substance is dissolved, the escaping tendency of the first liquid is lessened and its "activity" in solution may be thought of as the ratio of its vapor pressure p to the vapor pressure p_0 in the pure state. The ratio p/p_0 would be a satisfactory definition of activity except that the vapors are not ideal gases. Accordingly, G. N. Lewis invented the term *fugacity*, f, to express an idealized vapor pressure which meets the requirements of a perfect gas and is defined by the equation

$$F - F^0 = RT \ln \frac{f}{f^0} \tag{11}$$

where $F - F^0$ represents the change in free energy on passing from the standard state to the given state; f^0 is the idealized vapor pressure in the standard state, and f the idealized vapor pressure in the given state. The activity then is defined as

$$a = \frac{f}{f^0} \tag{12}$$

and

$$F - F^0 = RT \ln a. \tag{13}$$

The choice of a standard state is arbitrary and is determined by convenience. In the case of a *solvent*, the standard state is taken as the pure solvent and $a_1 = f_1/f_1^0$, where f_1^0 is the fugacity of the pure solvent. When Raoult's law is obeyed, as it is when the mol fraction of

the solvent N_1 approaches 1, the activity approaches the mol fraction, for under these conditions $p_1 = N_1 p_1^0$ as shown on p. 162.

In the case of a *solute*, the standard state is usually taken as a hypothetical state in which the pure solute (i.e. $N_2 = 1$) would have the properties which the solute possesses at infinite dilution. Then at any mol fraction the activity a_2 is defined by the equation

$$a_2 = \frac{f_2}{f_2^0}. \tag{14}$$

f_2^0 may be evaluated by determining, experimentally, the limit of f_2/N_2 as N_2 approaches zero. Frequently, also, f_2^0 is evaluated by extrapolating the ratio f_2/m to infinite dilution, where m is the molality.

In the case of *gases*, the idealized gas is taken as the standard state and $a = f$. In a perfect gas the activity is equal to the pressure, and in all gases the pressure approaches the activity as the pressure approaches zero. The fugacity of a gas may be determined from its pressure by correcting for the departure of the gas from ideal behavior at different pressures and in other ways,† but they cannot be discussed here. In most cases the error introduced by assuming the activities equal to the pressures are not large unless the pressure on the gas is considerably greater than atmospheric pressure.

The concept of activities is most useful in solutions, particularly in solutions of electrolytes.

Activities from Vapor Pressures. In the following table and in Fig. 150 are given the partial pressures, at 30°, of acetone and ether in solution. The vapors may be considered ideal so that pressures may be used in place of fugacities. The dotted lines show what the vapor pressures would be if the solutions were ideal. Considering the ether to be the solvent, the activity of ether at any mol fraction is merely the ratio of the partial pressure of ether to the vapor pressure of pure ether, 646 mm. For example, the partial pressure of ether at 0.2953 mol fraction ($N_{\text{acetone}} = 0.7047$) is 266 mm. and the activity of ether is 266/646 = 0.4119. If the solution were ideal, the activity at 0.2953 mol fraction would also be 0.2953.

Considering the acetone to be the solute, its activity may be calculated from its partial pressure with the help of Henry's law. It will be remembered that according to this law

$$p_2^* = N_2^* p_2^0$$

where p_2^* is the vapor pressure of the solute at mol fraction N_2^*

† Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," Chapter XVII.

VAPOR PRESSURE OF ACETONE-ETHER SOLUTIONS AT 30° C.*

Mol Fraction Acetone	Total Pressure mm.	Partial Pressure	
		Acetone	Ether
0	646.0	0	646.0
0.03867	645.3	21.8	632.5
0.1327	637.0	66.2	570.8
0.2509	616.9	106.7	510.2
0.4958	557.8	167.5	390.3
0.6507	502.7	201.2	301.5
0.7047	479.7	213 7	266.0
0.8381	409.6	243.1	166.5
0.9337	337.8	266.8	71.0
0.9528	326.0	270.7	55.3
0.9799	297.4	276.6	20.8
1.0	282.7	282.7	0

* Sameshima, J. Am. Chem. Soc., **40**, 1489 (1918).

where N_2^* is very small, and p_2^0 is the constant which is determined by experiment in dilute solutions. It is the slope of the vapor-pressure curve at infinite dilution; $p_2^0 = p_2^*/N_2^*$. Substituting p_2^*/N_2^* for p_2^0 and substituting p for f in equation (14),

$$a_2 = \frac{p_2}{p_2^0} = \frac{p_2}{p_2^*/N_2^*} = p_2 \frac{N_2^*}{p_2^*} \quad (15)$$

The ratio N_2^*/p_2^* is found to be 0.001697 by determining N_2/p_2 at various dilute solutions and extrapolating N_2/p_2 to infinite dilution.

Application of equation (15) shows further that the activity of acetone in 0.7074 mol fraction is $0.001697 \times 213.7 = 0.363$. The activity of ether is greater than the value calculated on the assumption of Raoult's law, i.e., the vapor pressure is above the dotted line. The activity of acetone is less than the value calculated on the assumption of Henry's law; i.e., the vapor pressure is below a tangent drawn at infinite dilution.

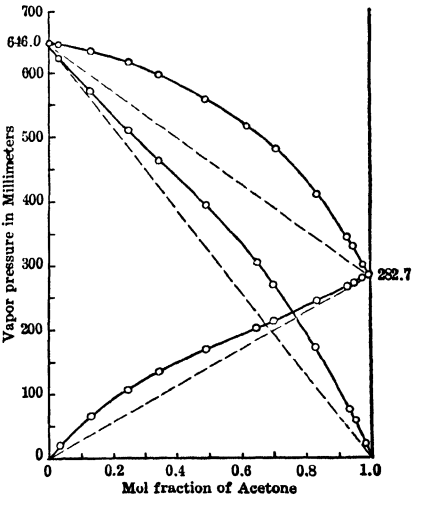


FIG. 150

Of course it is perfectly arbitrary to take ether as the solvent and acetone as the solute; equally useful results would be attained if the ether were considered the solute. In any calculations involving *change* in concentrations, the standard state cancels out.

Activities from Electromotive Force Measurements. Any measurement of the escaping tendency of the solute may be used for calculating the activity, and, in the case of electrolytes, electromotive force measurements offer a very accurate means of determining this escaping tendency. One of the best systems to study is that of thallium amalgam* because high concentrations can be obtained at room temperatures. In very dilute solutions the escaping tendency of the thallium from the mercury solution into an aqueous solution of thallous ions, as measured with a potentiometer, is proportional to the mol fraction N_2 of the thallium. In concentrated solutions the proportionality is no longer maintained (due in part to the formation of Tl_2Hg_5) as shown in the following paragraph.

The free energy change involved in transferring a mol of thallium at activity a_2' to another amalgam at activity a_2 is given by the equation

$$\Delta F = -n\boldsymbol{F}\boldsymbol{E} = RT \ln \frac{a_2}{a_2'}, \text{ or } E = -\frac{RT}{n\boldsymbol{F}} \ln \frac{a_2}{a_2'} \qquad (16)$$

and in dilute solutions

$$E = -\frac{RT}{n\boldsymbol{F}} \ln \frac{N_2}{N_2'}. \qquad (17)$$

When N_2 is less than 0.001, formula (17) gives voltages which agree well with the observed voltage. When N_2' is 0.03259 and N_2 is 0.01675, the calculated voltage is 0.0416 volt, whereas the observed voltage is 0.04555. When N_2' is 0.1680 and N_2 is 0.0986, $E_{\text{calc.}} = 0.0134$, and $E_{\text{obs.}} = 0.02434$. It is evident that formula (17) breaks down completely in concentrated solutions and that the escaping tendency is no longer proportional to the mol fraction.

The escaping tendency is, however, exactly proportional to the activity by definition of activity, and the only difficulty in calculating the activities from the electromotive force measurements lies in the measurements involving the reference state. If one could measure the voltage against an extremely dilute amalgam where the activity is equal to the mol fraction, the calculation would be simple, but there are practical difficulties, such as oxidation and contamination, which make these measurements unreliable. Accordingly, one amalgam, as dilute as is consistent with accuracy, is taken as the reference and measurements are made against a series of more concentrated amalgams.

* Richards and Daniels, J. Am. Chem. Soc., **41**, 1732 (1919).

The activities may then be obtained by extrapolation to infinite dilution; but simple extrapolation of the voltage is awkward and inaccurate at infinite dilution. Lewis and Randall* have shown how the extrapolation to infinite dilution may be made accurate by plotting instead of the voltage, a function of the voltage which is chosen so as to make the extrapolation definite at infinite dilution. Their calculations are given below:

At 20° C. equation (16) becomes

$$\log a_2 = \frac{-E}{0.05816} + \log a_2'; \tag{18}$$

subtracting log N_2 from both sides,

$$\log \frac{a_2}{N_2} = \left(\frac{-E}{0.05816} - \log N_2\right) + \log a_2'. \tag{19}$$

When N_2 approaches zero, a_2/N_2 approaches 1, according to the definition of the activity of a solute, and log a_2/N_2 approaches 0. Therefore, when the expression in parenthesis is plotted against N_2, as in Fig. 151, and the curve is extrapolated to the Y axis where $N_2 = 0$, the intercept gives directly the value of $-\log a_2'$, where a_2' is the activity of the thallium in the dilute amalgam arbitrarily taken as the reference amalgam. The difference between the value of this limiting ordinate, $-\log a_2'$, and the ordinates at different mol fraction gives at once the corresponding values of log a_2/N_2.

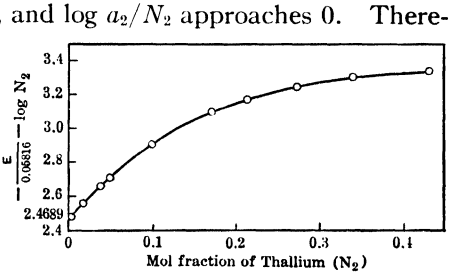


FIG. 151

Fig. 151 is constructed from the values of $-E$, using concentration cells in which amalgams of different mol fractions N_2 were measured against the most dilute amalgam used in the experiments ($N_2' = 0.00326$). These data are given in the first two columns of the following table, and by plotting $\left(\frac{-E}{0.05816} - \log N_2\right)$ against N_2 and extrapolating to $N_2 = 0$, $-\log a_2'$ is found to have the value 2.4689. Subtraction of this number from each of the values of the third column gives log a_2/N_2, and the corresponding antilogarithms, a_2/N_2, are recorded in the fourth column. The activities a_2 shown in the last column are readily obtained by multiplying a_2/N_2 by N_2.

* J. Am. Chem. Soc., **43**, 233 (1921); "Thermodynamics and the Free Energy of Chemical Substances," p. 265.

ACTIVITY OF THALLIUM IN AMALGAMS AT 20° C.

N_2	$-E$	$\frac{-E}{0.05816} - \log N_2$	$\frac{a_2}{N_2}$	a_2
0	$-\infty$	2.4689	1	0
0.003259	0	2.4869	1.042	0.003396
0.01675	0.04555	2.5592	1.231	0.02062
0.03723	0.07194	2.6660	1.574	0.05860
0.04856	0.08170	2.7184	1.776	0.08624
0.0986	0.11118	2.9177	2.811	0.2772
0.1680	0.13552	3.1045	4.321	0.7259
0.2074	0.14510	3.1780	5.118	1.061
0.2701	0.15667	3.2610	6.196	1.674
0.3361	0.16535	3.3159	7.031	2.363
0.4240	0.17352	3.3558	7.707	3.268

It will be noted that in the most dilute solutions the activities are about equal to the mol fractions but that in concentrated solutions the deviations are great, indicating that the solutions are far from ideal.

The concept of activities has been particularly fruitful in the study of the electrochemistry of aqueous solutions. Theoretically the activities of electrolytes can be obtained in a manner similar to that just described. If E represents the electromotive force of a cell of mean activity a, and E^0 represents the electromotive force of the cell in the standard state where a^0 equals unity, then as shown on p. 450:

$$-(E - E^0) = \frac{2RT}{nF} \ln a = 0.1183 \log a \qquad (20)$$

for a uni-univalent electrolyte at 25°. By subtracting 0.1183 log m from both sides and remembering that $a = \gamma m$,

$$E^0 - (E + 0.1183 \log m) = 0.1183 \log \gamma. \qquad (21)$$

At infinite dilution when m approaches zero, $\gamma = 1$ and $\log 1 = 0$, and

$$E^0 = E + 0.1183 \log m. \qquad (22)$$

Then E^0 may be evaluated graphically by plotting $(E + 0.1183 \log m)$ against m and extrapolating to $m = 0$. However, from a practical standpoint the electromotive force measurements are rarely accurate enough in very dilute solutions to obtain an accurate extrapolation, and it is necessary to use a function based on the Debye-Hückel theory which gives a straight line and permits accurate extrapolation to zero molality from more concentrated solutions.*

* This extrapolation is discussed by Hitchcock, J. Am. Chem. Soc. **50**, 2076 (1928).

The determination of the potential of the normal cadmium electrode and the activity coefficients of cadmium chloride solutions* may be taken as an example of a modern calculation of this type. The steps will be very briefly outlined.

The electromotive force of the cell

$$\mathrm{Cd},\ \mathrm{CdCl_2}(m),\ \mathrm{AgCl},\ \mathrm{Ag}$$

studied by Horsch can be expressed in terms of the equation

$$E_1 = E^0_1 - \frac{RT}{n\mathfrak{F}} \ln (4m^3\gamma^3).\dagger \tag{23}$$

In this equation, E_1 is the measured electromotive force of the cell, E^0_1 is the normal potential of the cell, m the concentration in mols per 1000 grams of solvent, and γ is the activity coefficient. Simplifying and changing to common logarithms, equation (23) becomes

$$E_1 = E^0_1 - 0.08873 \log (1.588\, m\gamma), \tag{24}$$

and rearranging

$$\log \gamma - E^0_1/0.08873 = -\left(\frac{E_1}{0.08873} + 0.2009 + \log m\right). \tag{25}$$

Following the procedure of Randall,‡ the right-hand side of equation (25) is plotted against the square root of the ionic strength μ (p. 479) and the resulting curve is extrapolated to infinite dilution in order to obtain E^0_1. The data derived from experiments by Horsch§ and the calculations are given in the following table.

m	$\sqrt{\mu}$	E_1	$(E_1/0.08873 + 0.2007 + \log m)$
0.0001000	0.01732	0.9597	7.0107
0.0001259	0.01943	0.9523	7.0407
0.0001585	0.02181	0.9445	7.0407
0.0001995	0.02446	0.9365	7.0507
0.0002512	0.02745	0.9282	7.0607
0.0003162	0.0308	0.9199	7.0707
0.0003981	0.0346	0.9117	7.0807
0.0005012	0.0388	0.9035	7.0807
0.0006310	0.0435	0.8954	7.0907
0.0007943	0.0488	0.8876	7.1007
0.001	0.0548	0.8801	7.1197

* Getman, J. Phys. Chem., **35**, 588 (1931).

† $4m^3\gamma^3$ is used for a bi-univalent electrolyte giving three ions. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 328 and p. 355.

‡ Trans. Faraday Soc., **23**, 505 (1927).

§ J. Am. Chem. Soc. **41**, 1787 (1919).

On plotting the values of $(E/0.08873 + 0.2007 + \log m)$ against $\sqrt{\mu}$ as shown in Fig. 152, the average straight line through the points thus obtained intersects the zero ordinate at 7.005, and on substituting this value in equation (25) we find $E^0_1 = 0.6215$ volt for the normal potential of the cell. Accurate measurements in these very dilute solutions are extremely difficult, and it is not yet possible to obtain points in this region which fall exactly on a straight line as demanded by theory. Changing from the silver chloride-silver electrode ($E = 0.2221$) to the normal hydrogen electrode as the reference electrode, the normal electrode potential E^0 of the cadmium electrode becomes

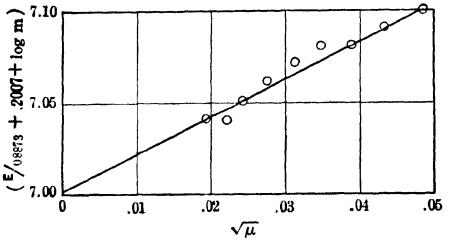


FIG. 152

$$-0.6215 + 0.2221 = -0.3994 \text{ volt.}^*$$

Having obtained E^0 for cadmium, the activity coefficient of cadmium chloride is readily obtained by direct measurement of the cadmium electrode in solutions of cadmium chloride of different molalities.

ACTIVITY COEFFICIENTS OF CADMIUM CHLORIDE

m	E_1	γ
0 0001	0 9567	0.969
0.0005	0.9050	0.802
0.001	0.8810	0 748
0.005	0.8280	0.592
0.01	0.8085	0.491
0.05	0.7688	0.277
0.1	0.7535	0.205
0.5	0.7209	0.096
1.0	0.7080	0.067

Activities of Solvent from Activities of Solute. In a binary mixture $N_1 + N_2 = 1$, where N_1 refers to the mol fraction of the solvent and N_2 refers to the mol fraction of the solute, and

$$dN_1 = -dN_2; \tag{26}$$

but since $d \ln N = dN/N$,

$$N_1 \, d \ln N_1 = -N_2 \, d \ln N_2. \tag{27}$$

Furthermore, it can be shown that for binary mixtures, free energy F

* The signs are determined by convention 4 on p. 431.

(or any additive property) is governed by the equation $N_1\,dF_1 + N_2\,dF_2 = 0$, and rearranging

$$dF_1 = -\frac{N_2}{N_1}dF_2. \tag{28}$$

Substituting in this equation, $RT \ln a$ for F

$$d \ln a_1 = -\frac{N_2}{N_1} d \ln a_2. \tag{29}$$

Subtracting equation (27) from equation (29),

$$d \ln \frac{a_1}{N_1} = -\frac{N_2}{N_1} d \ln \frac{a_2}{N_2} \tag{30}$$

Changing to common logarithms and integrating between infinite dilution and some specified mol fraction, we obtain equation (31). At infinite dilution the solution is essentially the same as the solvent and by definition the activity is then equal to the mol fraction. Then,

$$\frac{a_1^*}{N_1^*} = 1 \quad \text{and} \quad \log \frac{a_1^*}{N_1^*} = 0,$$

and integrating equation (30),

$$\log \frac{a_1}{N_1} = -\int_0^{N_2} \frac{N_2}{N_1} d \log \frac{a_2}{N_2}. \tag{31}$$

Now the integral on the right-hand side of the equation may be determined if the relation is known between N_2/N_1 and $\log a_2/N_2$, or it may be evaluated graphically by plotting N_2/N_1 against $\log a_2/N_2$ and finding the area under the curve. This method* can be used to determine the activities of mercury in a thallium amalgam at 20° C. from a knowledge of the activities of thallium (p. 516) as illustrated in Fig. 153. In the following table, the activities of thallium at various mol fractions are obtained from Fig. 151, and divided by the mol fractions as shown in the fourth column.

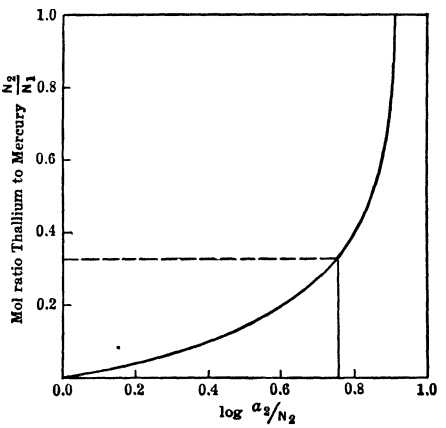


FIG. 153

* Lewis and Randall, J. Am. Chem. Soc., **43**, 233 (1921); " Thermodynamics and the Free Energy of Chemical Substances," p. 269.

ACTIVITIES OF MERCURY IN THALLIUM AMALGAMS

Mol Fraction Thallium N_2	Mol Fraction Mercury N_1	Mol Ratio N_2/N_1	Activity Tl / Mol Fract. Tl a_2/N_2	Activity Hg / Mol Fract. Hg a_1/N_1	Activity Hg a_1
0	1	0	1	1	1
0.005	0.995	0.00502	1.06	0.9998	0.995
0.01	0.99	0.0101	1.15	0.999	0.989
0.05	0.95	0.0526	1.80	0.986	0.937
0.1	0.90	0.111	2.84	0.950	0.855
0.2	0.80	0.250	4.98	0.866	0.693
0.3	0.70	0.428	6.60	0.790	0.553
0.4	....	....	7.57	.....	x
0.5	0.50	1.000	7.98	0.704	0.352

In Fig. 153 a dotted line is shown corresponding to a mol fraction of thallium of $\frac{1}{4}$ (mol ratio of $\frac{1}{3}$), and the activity of the mercury at this concentration is readily obtained by measuring the area under the curve out to the intersection with this dotted line. This area is equal to $-\log a_1/N_1$, from which a_1/N_1 and a_1 may readily be calculated. By this graphical method the data of the last two columns were obtained.

A similar method can be used for calculating the activity of the solute from that of the solvent, but here the curve approaches the axis asymptotically and the determination of the area is inaccurate. It is more satisfactory, then, to plot some arbitrary function of the activity of the solvent, which approaches zero at infinite dilution.* Such a method is particularly valuable in aqueous solutions where the activity of the solvent may be easily determined.

Activities from Freezing-Points. The activity of water is diminished by the addition of a solute, and this lessening of the escaping tendency leads to a lowering of the freezing-point (p. 174). Since freezing-point depressions can be measured more accurately than the other colligative properties of solutions they are often used for determining the activities of the solvent, and with an equation similar to (31), they are used also for determining the activities of the solute. In an earlier chapter (p. 177) it was shown that the concentration of a solute can be calculated approximately in a dilute solution when the freezing-point of the solution and that of the solvent are known; but in calculating activities with precision it is necessary to know the freezing-

* Lewis and Randall, " Thermodynamics and the Free Energy of Chemical Substances," p. 273.

points not only of the specified solution but also of several solutions to extreme dilutions. As usual, it is desirable to find some function which gives definite values at infinite dilution and which permits a straight-line extrapolation from moderately dilute solutions, because the experimental errors are very great in the extremely dilute solutions.

Such a function for aqueous solutions may be developed as follows:

θ = observed depression of the freezing-point.

θ/m = molal depression, i.e., the observed depression per mol at the given concentration.

λ = molal depression θ/m at infinite dilution = 1.858.

ν = number of ions or particles produced by one molecule (for non-electrolytes $\nu = 1$ and for NaCl $\nu = 2$, etc.).

At infinite dilution $\theta/\nu m$ approaches λ and $\theta/\nu\lambda m$ approaches 1. Then the function $(1 - \theta/\nu\lambda m)$ approaches zero at infinite dilution. Furthermore, a simple empirical relation has been found between this function and the molality as follows.*

$$\log\left(1 - \frac{\theta}{\nu\lambda m}\right) + \log \nu\lambda = \log\left(\nu\lambda - \frac{\theta}{m}\right) = \log b + \alpha \log m \qquad (32)$$

This equation holds within the limits of experimental accuracy in solutions below 0.01 m. By plotting $\log (\nu\lambda - \theta/m)$ against the logarithm of the molality a straight line is produced the slope of which gives α and the intercept of which gives $\log b$.

Such a graph is shown in Fig. 154 where the calculations of Harned† are given. From this graph it is found that for sodium chloride $\alpha = 0.413$ and $b = 0.720$.

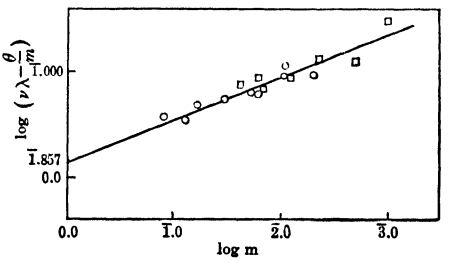


FIG. 154

By a treatment too complicated to be given here it can be shown‡ that these constants are related to the activity coefficient γ by the following equation

$$\log \gamma = \frac{-b(\alpha + 1)m^{\alpha}}{2.303\,\nu\lambda\alpha} = -\beta m^{\alpha}. \qquad (33)$$

In the case of aqueous solutions of sodium chloride,

$$\log \gamma = -0.288 m^{0.413}. \qquad (34)$$

* Lewis and Linhart, J. Am. Chem. Soc., **41**, 1852 (1919).

† J. Am. Chem. Soc., **44**, 252 (1922).

‡ Taylor, " Treatise on Physical Chemistry," p. 767; Lewis and Randall, " Thermodynamics and the Free Energy of Chemical Substances," pp. 284–286, 342–344.

With this formula the activity coefficients of sodium chloride have been calculated at various concentrations, and with similar formulas most of the data on the activity coefficients of strong electrolytes have been determined (p. 451). These values have been used extensively in determining the normal electrode potentials (p. 441).*

Entropy. It has been shown (p. 132) that the tendency of a system to undergo spontaneous change may be measured by the decrease in free energy, i.e., by the maximum useful work which can be obtained through some type of ordered motion. This tendency to change may be studied also in another way by centering attention on the degree to which the system has approached a state of equilibrium.

Entropy is a measure of the extent to which a system is run down. A system increases in entropy when it passes into a more probable state (a more random state) where the motion is less ordered. The second law of thermodynamics may now be stated in still another way as follows. *In any spontaneous process the entropy of the system as a whole tends to increase.*

A quantitative expression for entropy change may be developed from the mathematical expression of the second law where w_{max} represents the maximum work and q_{rev} represents the heat absorbed in a reversible process.

$$w_{max} = q_{rev}\frac{T_2 - T_1}{T_2} = q_{rev}\left(\frac{T_2}{T_2}\right) - q_{rev}\left(\frac{T_1}{T_2}\right) = q_{rev} - \left(\frac{q_{rev}}{T_2}\right)T_1. \quad (35)$$

$$q_{rev} = w_{max} + \left(\frac{q_{rev}}{T_2}\right)T_1. \quad (36)$$

In this equation $(q_{rev}/T_2)T_1$ represents that part of the heat which cannot do work, or in other words it represents the unavailable energy.

The quantity q_{rev}/T is defined as entropy change. Entropy is represented by the symbol S, and in an isothermal, reversible process the heat absorbed divided by the absolute temperature gives directly the increase in entropy,

$$\Delta S = S_2 - S_1 = \frac{q_{rev}}{T}. \quad (37)$$

Entropy units are expressed as calories divided by absolute temperature. The following example will serve to illustrate the application of the change of entropy accompanying a physical change. Solid and

* Further material on the determination of activities from freezing-point measurements may be found in the following references: Randall and Vanselow, J. Am. Chem. Soc., **46**, 2418 (1924); Scatchard, J. Am. Chem. Soc., **47**, 648 (1925); Getman, J. Phys. Chem., **33**, 1781 (1929); **34**, 1454 (1930); Harkins, J. Am. Chem. Soc., **53**, 852 (1931); Robertson and La Mer, J. Phys. Chem., **35**, 1953 (1931).

liquid mercury are in equilibrium at the melting-point 234.1° on the absolute scale, and the transition from one phase to the other is strictly reversible, the direction of change being conditioned by infinitesimal changes in temperature or pressure. The heat of fusion is 560 calories per mol and the temperature remains constant, hence the increase in entropy in the process

$$\mathrm{Hg_{solid}} \rightarrow \mathrm{Hg_{liquid}},$$

is

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{560}{234.1} = 2.39 \text{ cal. per degree.}$$

The molal entropy of liquid mercury exceeds that of solid mercury by 2.39 entropy units at the freezing-point.

It must be emphasized that entropy changes can be calculated in this way only if the heat is measured under reversible conditions. For example, if supercooled water at $-5°$ changes spontaneously to ice at $-5°$ the entropy change is not equal to the heat divided by the absolute temperature because the process is not reversible. Ice at $-5°$ cannot be converted isothermally at ordinary pressures into water at $-5°$ by infinitesimal changes in temperature or pressure. The entropy change may be obtained, however, by heating the water reversibly to 0°, freezing the water reversibly at 0° and cooling the ice reversibly to $-5°$.

Change of Entropy with Temperature. If dT is the infinitesimal increase in the temperature of a system whose heat capacity is C, due to the absorption of a quantity of heat, q, then

$$q_{\text{rev}} = C\,dT.$$

But

$$dS = q_{\text{rev}}/T,$$

and therefore

$$dS = C\frac{dT}{T}. \tag{38}$$

At constant volume we have

$$dS = C_v\frac{dT}{T} = C_v\,d\ln T, \tag{39}$$

and integrating between limits T_2 and T_1 on the assumption that C_v is constant,

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} C_v\,d\ln T, \tag{40}$$

or

$$S_2 - S_1 = C_v \ln T_2/T_1 = 2.303\,C_v \log\frac{T_2}{T_1}. \tag{41}$$

In the same way at constant pressure,

$$S_2 - S_1 = C_p \ln\frac{T_2}{T_1} = 2.303\,C_p \log\frac{T_2}{T_1}. \tag{42}$$

As an example of the application of these equations we may calculate the increase in entropy produced by heating a mol of mercury at constant pressure from its melting-point 234.1° K. to 298.1° K. The value of C_p is taken as 6.7. Then

$$\Delta S = S_2 - S_1 = 2.303 \times 6.7 \log \frac{298.1}{234.1} = 1.62.$$

Change of Entropy in a Perfect Gas. According to the first law of thermodynamics, the heat absorbed by a perfect gas for an infinitesimal change of internal energy is

$$q = dU + p\,dv.$$

But

$$dS = q_{\text{rev}}/T,$$

hence it follows that

$$dS = \frac{dU + p\,dv}{T},$$

and

$$dS = \frac{C_v\,dT + p\,dv}{T}. \tag{43}$$

Integrating on the assumption that C_v is independent of temperature, and substituting RT/v for p, we have

$$\int dS = C_v \int \frac{dT}{T} + R \int \frac{dv}{v} + \text{constant}. \tag{44}$$

or

$$S = C_v \ln T + R \ln v + \text{constant}. \tag{45}$$

If 1 mol of gas expands isothermally from volume v_1, to volume v_2, the increase in entropy is

$$\Delta S = S_2 - S_1 = R \ln v_2/v_1. \tag{46}$$

The Third Law of Thermodynamics. It has been indicated that the greater the randomness of a system the greater is the entropy S. The random motion of atoms and molecules, due to heat, decreases as the temperature is lowered and the entropy accordingly decreases. A crystal with its orderly arrangement of atoms in the crystal lattice should also have a comparatively small entropy content.

According to the *third law of thermodynamics, the entropy of a crystal at the absolute zero is zero.* The importance of this law is evident at once, for it makes possible the determination of absolute entropies. The increase in entropy involved in heating from absolute zero to any specified temperature may be calculated with the help of equation (38), and according to the third law this increase in entropy is the absolute entropy. Tables of entropy have been prepared from specific heat

data, and from these entropies the entropy changes in chemical reactions can be determined.

There is as yet no conclusive proof of the validity of the third law, but it has been checked and cross-checked in many different ways. In the following section, for example, it will be shown that the entropy calculations based on the third law agree well with the entropy values as calculated from measurements of free energy and heat content. The idea of the third law was suggested in 1902 by Richards,* who found that the temperature coefficient of voltage of most galvanic cells approached zero at low temperatures. This derivative of free energy decrease with respect to temperature can be shown to be equal to the entropy increase. Nernst developed the third law, and this branch of thermodynamics is sometimes referred to as the Nernst heat theorem.† More recent developments have been due to Nernst,‡ Lewis§ and his associates, and Eucken,¶ and Parks.||

The determination of absolute entropies is illustrated with the data on silver shown in the following table and plotted in Fig. 155.

HEAT CAPACITY OF SILVER**

T	Log T	C_v	T	Log T	C_v
13.5	1.130	0.11 (calc.)	51.4	1.7110	2.81
17.0	1.230	0.21 (calc.)	53.8	1.7308	2.97
26.9	1.430	0.84 (calc.)	77.0	1.8865	4.07
35.0	1.5441	1.59	100	2.0000	4.72
39.1	1.5922	1.92	200	2.3010	5.60
42.9	1.6325	2.22	273	2.4362	5.77
45.5	1.6580	2.43	535	2.7284	5.90
			589	2.7701	5 92

** Nernst and Lindemann, Z. Electrochem., **17**, 817 (1911).

Taking the entropy at 0° K. as zero, according to the third law, and applying equation (40), the absolute entropy at 298° is given by the equation

$$S_{v,298} = 2.303 \int_0^{298} C_v \, d \log T. \qquad (47)$$

* Z. physik. Chem., **42**, 129 (1902).

† Nachr. kgl. Ges. Wiss. Göttingen Math. Physik. Klasse (1906) 1.

‡ Nernst, "Die Theoretischem und Experimentallen Grundlagen des Neuen Wärmesatzes."

§ Lewis, Gibson and Latimer, J. Chem. Am. Soc., **44**, 1008 (1922).

¶ Eucken, Z. physik. **29**, 1 (1924).

|| Parks and co-workers, J. Am. Chem. Soc., **47**, 338 (1925); **48**, 1506, 2788 (1926); **52**, 1032, 1547, 3241, 4381 (1930).

The mathematical relation between C_v and log T is not known (except at very low temperatures), and so it is necessary to evaluate the integral by graphical means. The area $\left(\int y\,dx\right)$ is determined by plotting C_v against log T accurately, and counting the squares under the curve between log 0 and log 298, this area in turn being multiplied by the conversion factor of natural logarithms. In the case of silver, the value of $S_{v,298}$ obtained by evaluating this area is 10.0 entropy units (calories per degree).

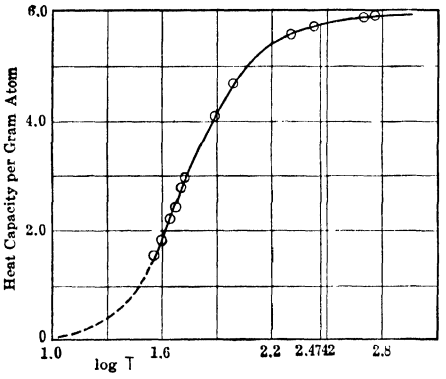


FIG. 155

Specific heat measurements have been made with special electrical calorimeters on many substances down to liquid air temperatures, and in some cases down to the boiling-point of hydrogen. The extrapolation of the curve to absolute zero does not involve very large errors, and fortunately, in the region of absolute zero, the specific heat-temperature curve can be calculated with fair accuracy from formulas* which rest partly on theoretical foundations (Chapter XXIV).

In determining entropies from specific heat curves it is necessary to have the system always in a state of equilibrium so that the input at each temperature is a strictly reversible process. This requirement frequently demands a slow rate of heating. Another restriction depends on the fact that an increase in entropy is produced by mixing two substances, and if the entropy of these pure substances is zero at 0° K. the mixture cannot be zero also. Accordingly the third law is restricted to pure crystals, but often it may be applied, with only small errors,† to solutions and glasses.

In case there is a change of state, or a transition from one crystalline

* Einstein, Ann. Physik, (4) **22**, 180 (1907); Debye, Ann. Physik, (4) **39**, 789 (1912).

† An interesting case is that of hydrogen, which exists in two forms, ortho and para, each having different specific heats as described in Chapter XXIV. Thermodynamical calculations persisted in showing that the entropy of hydrogen was too low by an appreciable amount, and it is now known that an entropy increase of this magnitude, due to the change from one form to the other, does actually occur just above the absolute zero. The change comes at such a low temperature in the case of hydrogen that it was missed in the experimental measurements.

form to another, the heat absorbed in the change must be divided by the temperature at which the change takes place, and added to the entropy as calculated from the specific-heat curve.

The following table gives the absolute entropies at constant pressure of a number of elements and compounds obtained from these specific-heat measurements at low temperatures.

TABLE OF ATOMIC AND MOLECULAR ENTROPIES AT 25° C.

Entropy per Gram-atom		Entropy per Gram-molecule	
Hydrogen ($\frac{1}{2}$ H_2)	15.6	Methanol	32.6
Helium	29.8	Maleic acid	38.1
Carbon (diamond)	0.6	Fumaric acid	39.7
Carbon (graphite)	1.3	Benzene	41.9
Nitrogen ($\frac{1}{2}$ N_2)	23.0	Ethanol	42.3
Oxygen ($\frac{1}{2}$ O_2)	24 0	*tertiary*-Butanol	47.2
Aluminum	6 8	*cyclo*-Hexane	49.2
Sulphur (rhombic)	7.6	Toluene	52.4
Sulphur (monoclinic)	7.8	*n*-Butanol	60.2
Chlorine ($\frac{1}{2}$ Cl_2)	26.3	*n*-Hexane	60.8
Silver	10 2	Ethyl benzene	61.2
Mercury (liquid)	17.8	Ethyl ether	67.7
Mercury (gas)	41.5	*n*-Heptane	78.9

Entropy and Free Energy. The relation between the entropy change and free energy change in an isothermal reaction may be defined by the following equation,

$$\Delta F = \Delta H - T\,\Delta S. \qquad (48)$$

It is seen from this equation that when there is no change in entropy during a reaction (i.e., the products have the same entropy as the reacting substances) the decrease in heat content is equal to the decrease in free energy. Usually, however, there is an entropy change during the reaction and the decrease in free energy is greater or less than the decrease in heat content depending on the sign of ΔS. This relation was shown on p. 430, where the difference between free energy change and heat of reaction was attributed to the heat absorbed from the surroundings by the reversible process. But this quantity divided by the absolute temperature is defined as the entropy increase (p. 522).

Since entropies and heats of reaction can be determined from calorimetric measurements alone, it is now possible to calculate free energy changes and equilibrium constants without involving any chemical measurements. This determination of chemical affinities from ther-

mal data is a goal which has been eagerly sought by many investigators during the past fifty years.

The calculation of chemical equilibria from entropy data using equations (48) and (1) is particularly valuable in organic chemistry because frequently no other method is available. Often the reaction rates are so very slow that direct measurements of equilibrium are impossible. Benzene may be taken as an example. Benzene appears to be a stable substance at room temperature and carbon and hydrogen appear to be unreactive toward each other. It is not possible then to measure the equilibrium among the three but it may be determined indirectly from the entropies and the heat of reaction (problem 28).

This method for calculating equilibria may be illustrated by the reaction

$$C_{\text{graphite}} + 2\,H_2\,(g) = CH_4\,(g) \quad \Delta H_{873} = -21{,}045$$

The entropies of C_{graphite}, H_2 and CH_4 are 4.8, 38.9 and 56.6 respectively at 873° K.

$$\Delta S = S_{\text{products}} - S_{\text{reactants}} = 56.6 - (38.9 \times 2 + 4.8) = -26$$

$$\Delta F^0 = \Delta H - T\,\Delta S = -21{,}045 - (873 \times (-26)) = 1653$$

Since

$$\Delta F^0 = -RT \ln K,$$

$$K = 0.39.$$

This method of calculating equilibrium constants from entropy data has come into extensive industrial use, particularly in determining whether or not a given synthesis is thermodynamically possible. Further examples may be obtained from the recent literature.* One of the greatest difficulties appears to be in the heavy demands made on the accuracy of the measurements of ΔH. These values are usually obtained from differences between large quantities, and a small error in one of these values makes a large error in the value of ΔF. In the calculation of the methanol equilibrium, for example, an error of 0.1 per cent in one of the values for the heat of combustion makes an error of 35 per cent in the equilibrium constant. As a rule, a greater error can be tolerated in the entropy measurements than in the measurements which determine the values of the heat content.

Nernst's Constants. For the determination of chemical equilibria the following methods have been described: (*a*) direct experimental measurement, (*b*) ratio of specific reaction rates, (*c*) calculation from

* Kelley, Methanol Synthesis, Ind. Eng. Chem., **21**, 353 (1929); Storch, Entropy and Free Energy of Methane, J. Am. Chem. Soc., **53**, 1266 (1931); Parks and coworkers, The Entropies of Organic Compounds, J. Am. Chem. Soc., **52**, 4381 (1930), and earlier papers.

free energy data, (*d*) calculation from entropy data. The use of Nernst's conventional constants offers still another method, which is considerably less accurate than the others but quite simple. Although the constants are largely empirical they permit fairly accurate estimates of an equilibrium constant and in many cases where data are lacking they constitute the only method available.

Nernst's equation which is an important part of his heat theorem* is as follows:

$$\log K_p = \frac{-\Delta H}{4.58\,T} + \Sigma n\ 1.75 \log T + \Sigma(nc), \qquad (49)$$

where ΔH is the heat of reaction at the temperature T, Σn is the algebraic sum of the number of gaseous mols (i.e., mols of products minus mols of reactants), and $\Sigma(nc)$ is the algebraic sum of the Nernst constants (i.e., constants for gaseous products minus constants for gaseous reactants), n referring to the number of mols of each gas involved.† The equation was originally developed by integrating the fundamental equation $d \log K/dT = \Delta H/RT^2$ after substituting for ΔH its equivalent $\Delta H_0 + aT + \frac{1}{2}bT^2 + \frac{1}{3}cT^3 + \cdots$ and evaluating the integration constants from existing experimental data.

The Nernst constants for a few substances are as follows:

NERNST'S CONSTANTS

H_2 ..... 1.6	HCl 3.0	N_2O ... 3.3	C_2H_4 ..... 2.8
N_2 ..... 2.6	CO 3.5	NH_3 . 3.3	C_2H_6 ..... 2.6
O_2 ..... 2.8	CO_2 ..... 3.2	H_2O . 3.6	C_6H_6 ..... 3.0
Cl_2 ..... 3.1	NO 3.5	CH_4 ..... 2.8	CCl_4 ..... 3.4

These constants and formula (49) apply only to substances in the gaseous state. They can be applied to heterogeneous systems if all the materials except the gases are disregarded.

Applying this method to the calculation of the equilibrium of the reaction

$$C_{\text{graphite}} + 2\,H_2\,(g) = CH_4\,(g)$$
$$\Delta H_{873} = -21{,}045 \qquad \Sigma n = 1 - 2 = -1$$
$$\Sigma(nc) = 2.8 - (2 \times 1.6) = -0.4.$$

* Nernst, Theoretical Chemistry," Book V.

† Nernst's conventions are opposite to some of those employed here, and when studying the German articles it must be remembered that the reactants are usually placed in the numerator, giving $K_{\text{Nernst}} = 1/K$, and $\Sigma n_{\text{Nernst}} = -\Sigma n$. The signs of equation (49) must then be changed.

Substituting in equation (49),

$$\log K = \frac{21{,}045}{4.58 \times 873} - 1.75 \log 873 - 0.4 = -0.283$$

$$K = 0.52.$$

This value is in agreement with that obtained from entropy data as just shown.

Partial Molal Quantities. The concept of partial molal quantities, developed by G. N. Lewis, has helped materially in placing the study of solutions on an exact basis. For example, when a mol (32 grams) of methyl alcohol is added to a small quantity of water the change in volume produced on mixing is not the same as when the alcohol is added to a large quantity of water. The volume depends on the concentration, and since the concentration changes during the mixing the measurements are complicated in a manner which was not realized in the early work on solutions. The obvious and simple way of handling this problem is to use the methods of partial differentiation and record the change produced by the addition of an infinitesimal quantity of the solute. The partial molal volume $\overline{V}$, is defined so that

$$\overline{V} = \frac{\partial V}{\partial n}. \tag{50}$$

It is the rate of change in volume produced by the addition of solute to the solution. The partial molal volume of the solute $\overline{V}_2$ changes with the concentration, and it can be visualized as the increase in volume produced by adding 1 mol of the solute to a large quantity of the solution, a quantity so large in fact that the addition of the 1 mol of solute does not increase appreciably the concentration of the solution. For example, a mol of methanol weighs 32.0 grams and occupies 40.45 cubic centimeters. When it is added to a large reservoir of pure methanol the volume is increased 40.45 cubic centimeters, but when it is added to a large reservoir of a solution containing 0.2 mol fraction of methanol and 0.8 mol fraction of water the increase is only 37.77 cubic centimeters. An obvious method for determining the partial molal volume of a solute consists in plotting the volume of the solution against the number of mols of solute contained in 1000 grams of the solvent,

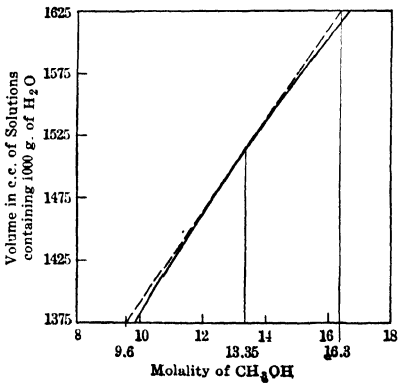


FIG. 156

i.e., against the molality, and determining the slope of the curve as shown in Fig. 156. The slope of the curve $\partial V/\partial n_2$ at any molality gives the rate of change in volume with the mols of solute added, but this is by definition the partial molal volume of the solute. In Fig. 156 the tangent is drawn to the curve at a molality of 13.35, corresponding to a mol fraction of 0.20, and it is found to have a slope of (1625 − 1375)/(16.30 − 9.60) or 37.3, which is the partial molal volume of the methanol at this molality.

The method just given illustrates the meaning of the partial molal quantities, but it is possible to obtain greater accuracy by other methods.

The method of intercepts is illustrated in Fig. 157, where the specific volume (the volume of 1 gram of the solution, or the reciprocal of the density) is plotted against the percentage by weight. It can be shown by simple methods of analytical geometry and differential calculus* that the intercepts on the two ordinates pure water (0 per cent methanol) and pure methanol (100 per cent methanol) give at once the partial specific volumes of the two components in the solution at the composition corresponding to the point of tangency. The partial specific volumes are converted into partial molal volumes by merely multiplying by the molecular weights.

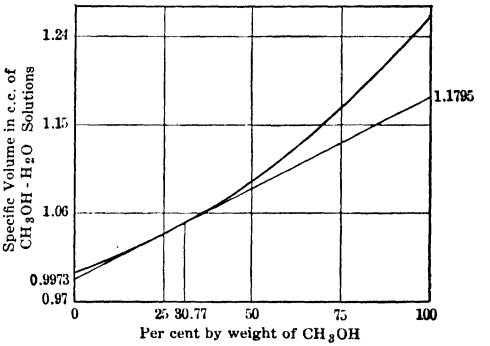


FIG. 157

The data and calculations on which Fig. 157 is based are given in the following table.

In Fig. 157 a tangent is drawn at a composition of 30.77 per cent (mol fraction = 0.20) and it intersects the ordinates at 0.9973 and 1.1795.

The partial molal volume of water is $18.02 \times 0.9973 = 17.97$, and that of methanol is $32.03 \times 1.1795 = 37.7$, a value which agrees within the errors of graphing on a small scale with that obtained by the other method shown in Fig. 156, namely, 37.3.†

* Roozeboom, " Die heterogen Gleichgewichte," II, p. 288 (1904); Lewis and Randall, " Thermodynamics and the Free Energy of Chemical Substances," p. 38.

† A more accurate method which reduces errors of graphing is given by Lewis and Randall in " Thermodynamics and the Free Energy of Chemical Substances," p. 37.

PARTIAL MOLAL VOLUMES OF METHANOL AND WATER
Method of Intercepts

Mol Fraction CH_3OH	Percentage CH_3OH	Density Solution	Specific Volume	Molal Volume	Partial Molal Volume	
					H_2O	CH_3OH
0	0	0.9982	1.002	18.05	.....	.....
.20	30.77	0.9503	1.053	21.93	17.97	37.77
.40	54.24	0.9068	1.103	26.05	17.35	39.01
.60	72.73	0.8647	1.157	30.56	16.67	39.82
.80	87.66	0.8268	1.210	35.34	15.35	40.38
1.00	100.0	0.7917	1.263	40.45	.....	.....

Other properties such as partial molal heat capacities, or partial molal heat contents, may be determined in the same way as the partial molal volumes.

After the partial molal volumes (or other properties) have been determined, the volume of the whole solution can be obtained at any concentration by direct addition, as shown by the equation

$$n_1\overline{V}_1 + n_2\overline{V}_2 + n_3\overline{V}_3 + \cdots = V, \qquad (51)$$

where V is the volume of the whole solution, and where n refers to the number of mols, and $\overline{V}$ to the corresponding partial molal volumes.

REFERENCES

Thermodynamics and the Free Energy of Chemical Substances. Lewis and Randall.
Treatise on Physical Chemistry, Chapters XII and XVII. Taylor.
Thermodynamics and Chemistry. MacDougall.
Thermodynamik. Schottky.
J. Chem. Education, **8**, 1062 (1931). Randall.
Statistical Mechanics. Fowler.

PROBLEMS

1. Calculate ΔF^0_{298} for the reaction

$$C\ (\text{graphite}) + O_2\ (g) + Cl_2\ (g) = COCl_2\ (g)$$

from the following data:

$C\ (\text{graphite}) + O_2\ (g) = CO_2\ (g)$ $\quad \Delta F^0_{298} = -94{,}260$ cal.
$C\ (\text{graphite}) + CO_2\ (g) = 2\,CO\ (g)$ $\quad \Delta F^0_{298} = 29{,}240$ cal.
$CO\ (g) + Cl_2\ (g) = COCl_2\ (g)$ $\quad \Delta F^0_{298} = -16{,}260$ cal.

Ans. **−48,770 cal.**

2. $N_2O_4 \rightarrow 2\ NO_2 \qquad \Delta F^0_{298} = 1154$ cal.
Calculate ΔF_{298} for the following reactions, assuming that the pressures are equal to the fugacities
(*a*) N_2O_4 (1 atmos.) = 2 NO_2 (1 atmos.)
(*b*) N_2O_4 (10 atmos.) = 2 NO_2 (1 atmos.)
(*c*) N_2O_4 (1 atmos.) = 2 NO_2 (10 atmos.)
(*d*) Which of these reactions will occur spontaneously?

3. Determine (*a*) ΔF^0 and (*b*) the equilibrium constant at 298° of the reaction

$$CO_2 + H_2 = H_2O + CO$$

from the following data:

$CO_2\ (g) + 4\ H_2\ (g) = CH_4\ (g) + 2\ H_2O\ (g) \qquad \Delta F^0_{298} = -26{,}912$
$2\ H_2\ (g) + O_2\ (g) = 2\ H_2O\ (g) \qquad \Delta F^0_{298} = -109{,}014$
$2\ C\ (s) + O_2\ (g) = 2\ CO\ (g) \qquad \Delta F^0_{298} = -65{,}020$
$C\ (s) + 2\ H_2\ (g) = CH_4\ (g) \qquad \Delta F^0_{298} = -12{,}206$

Ans. (*b*) 5.5×10^{-6}.

4. $3\ NO_2\ (g) + H_2O\ (g) = NO\ (g) + 2\ HNO_3\ (g) \quad \Delta F^0_{298} = 3190$ cal.
(*a*) What is the free energy of formation of HNO_3 (*g*)?
(*b*) Determine ΔF^0_{298} and K for the reaction

$$H_2O\ (g) + 2\ NO_2\ (g) + \tfrac{1}{2}\ O_2\ (g) = 2\ HNO_3\ (g)$$

Ans. (*b*) $\Delta F^0_{298} = -5183$ cal.

5. $3\ NO_2\ (g) + H_2O\ (g) = NO\ (g) + 2\ HNO_3\ (g) \quad \Delta F^0_{298} = 3190$ cal.
Since ΔF^0 has a positive value, the reactants at unit activity (practically 1 atmosphere partial pressure) will not react spontaneously to give the products, each at unit activity. What is the lowest pressure of NO_2 which will react with water at 0.01 atmosphere to give nitric oxide and nitric acid, each at 0.01 atmosphere.

6. At 377° C., $R \ln K = -16.44$ for the reaction

$$CH_4 + 2\ H_2O = CO_2 + 4\ H_2$$

At 25° C. for this reaction $\Delta H = 39{,}432$. Construct the equation showing the variation of ΔF^0 with temperature using the following specific heat data:

$C_{p_{H_2}} = 6.85 + 0.28 \times 10^{-3}\ T + 0.22 \times 10^{-6} T^2$
$C_{p_{H_2O}} = 8.22 + 0.15 \times 10^{-3}\ T + 1.34 \times 10^{-6} T^2$
$C_{p_{CO_2}} = 7.70 + 5.30 \times 10^{-3}\ T - 0.83 \times 10^{-6} T^2$
$C_{p_{CH_4}} = 4.38 + 14.17 \times 10^{-3}\ T$

7. (*a*) Calculate ΔF^0 at 1810° K. from the data given on p. 510 for the reaction

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

(*b*) What is the equilibrium constant at this temperature?
(*c*) To what extent is HCl dissociated at this temperature?

Ans. (*c*) 0.17 per cent.

8. The free energy of the reaction

$$CO\ (g) + Cl_2\ (g) = COCl_2\ (g)$$

can be represented by the equation

$$\Delta F^0 = -24{,}100 + 4\ T \ln T + 3.5\ T$$

Calculate the partial pressure of carbon monoxide in equilibrium with phosgene at 100° C. and a total pressure of one atmosphere, assuming that the gases are perfect gases. *Ans.* 8.19×10^{-5} atm.

9. From the table, calculate the activities of the solvent ether and the solute acetone at a mol fraction of acetone of 0.1327 at 30°.

Ans. $a_1 = 0.884$. $a_2 = 0.1124$.

10. From the table, calculate the activities of the solvent ether and the solute acetone at a mol fraction of acetone of 0.4958 at 30°.

11. What is the value of x in the table on page 520 as obtained by plotting Fig. 153 on a large scale and integrating graphically?

12. The electromotive force of various cells composed of electrodes of a pure metal and the metal in an alloy in contact with a fused salt of the metal has been measured. For the cell

$$\text{Cd, Cd}^{++}\text{, Cd–Sn}$$

at 483°, the following results were obtained:

Mol fraction Cd in alloy (N_1)	0.0835	0.222	0.451	0.630	0.816
EMF in volts	0.0632	0.0355	0.0185	0.0111	0.0053

Calculate $\log \frac{a_1}{N_1}$ for each mol fraction, and estimate

$$\log \frac{a_2}{N_2} \text{ at } N_1 = N_2 = 0.5.$$

Since one electrode is a pure metal, Cd, its activity is taken as unity.

13. Calculate the activity coefficients of sodium chloride in aqueous solutions at 0.001 molal, and 0.05 molal and compare with the values given on page 451.

14. The freezing-points θ of solutions of potassium chloride in water at various molalities are as follows:

m	0.11679	0.05818	0.03170	0.01648	0.01023	0.00963
θ	0.4014	0.2031	0.1122	0.0590	0.03674	0.0348

Determine graphically b and α in equation (33) and calculate the activities γ at $m = 0.001$ and $m = 0.05$. These values may be checked with those given in tables in Chapter XVII.

15. (*a*) Solid methane has a transition point at 20.4° K.; the heat of transition is 18.1 cal/mol.

(*b*) The heat of fusion at the melting-point 90.6° K. is 224.0 cal/mol.

(*c*) The heat of vaporization at 111.8° K. is 1968 cal/mol. Compute the entropy change in each of these processes. *Ans.* (*a*) 0.89.

16. Compute the increase in entropy when one mol of bromine is transformed from the solid state at its melting-point, 7.32° C., to vapor at its boiling-point 61.55° C., having given the following data: — Specific heat of liquid bromine, 0.107, heat of fusion 16.185 cal. per gram and the heat of vaporization 43.69 cal. per gram.

Ans. 33.13 cal/degree.

17. What is the entropy increase when one mol of mercury is subjected to the following operations?

(*a*) Heated from −80° C. to −40° C.
(*b*) Melted at −40° C.
(*c*) Heated from −40° C. to 360° C.
(*d*) Vaporized at 360° C.

The average specific heat of solid mercury is 0.0315 and that of liquid mercury is 0.033. The heat of fusion is 2.8 calories per gram and the heat of vaporization is 65 calories per gram.

18. By integration of equation (38), find the entropy change ΔS_p on heating 1 mol of methane at constant pressure from its boiling-point 111.8° K. to 298.1° K., knowing that in this temperature range

$$C_p = 5.90 + 9.60 \times 10^{-3}\, T$$

Ans. 7.52.

19. Plot C_v against log T on a large scale and determine S_v for silver at (*a*) 298° K. and (*b*) 600° K.

20. Calculate the entropy change at 25° in the reaction

$$CH_4 + 2\,H_2O = CO_2 + 4\,H_2$$

knowing that $\Delta H_{298} = 39{,}432$, and

$$\Delta F^0 = 35{,}573 - 14.28\, T \ln T + 4.03 \times 10^{-3}\, T^2 + 0.44 \times 10^{-6}\, T^3 + 51.5\, T$$

Ans. 40.1.

21. (*a*) What is the free energy change involved when 32 grams of monoclinic sulphur changes into rhombic sulphur at 25° C.? The entropy of rhombic sulphur is 7.6 and that of monoclinic sulphur is 7.8. When 32 grams of rhombic sulphur is oxidized 82 calories less heat is evolved than when 32 grams monoclinic sulphur is oxidized.

(*b*) What is the ratio of the vapor pressure of rhombic sulphur to the vapor pressure of monoclinic sulphur at 25°?

22. Rhombic and monoclinic sulphur exist in a state of equilibrium at the transition temperature 95° C. Calculate ΔF^0 for the transition from monoclinic into rhombic sulphur at 25° C.

For rhombic sulphur $C_p = 4.12 + 0.0047\, T$
For monoclinic sulphur $C_p = 3.62 + 0.0072\, T$
$\Delta H_{298} = -82$ cal.

Compare your answer with that of Prob. 21.

23. What is the entropy change when 1 mol of supercooled water at −5° changes into ice at −5° C.?

$\Delta H_{273} = -80$ cals. per gram.
C_p for water = 1.01 C_p for ice = 0.49

24. In a study of the formation of methane from hydrogen and graphite Storch used the following data:

For hydrogen (H_2) $C_p = 6.85 + 0.00028\, T + 0.00000022\, T^2$
$S_{298} = 31.23$
For graphite (C) $C_p = 1.22 + 0.00489\, T - 0.00000111\, T^2$
$S_{298} = 1.3$
For methane (CH_4) $C_p = 4.38 + 0.01417\, T$
$S_{298} = 43.39$.

(*a*) Calculate the entropies of each of these substances at 873° K.
(*b*) Calculate ΔS_{873} for the reaction C (graphite) + 2 H_2 (*g*) → CH_4 (*g*).

Ans. (*a*) Hydrogen $S_{873} = 38.9$. Graphite $S_{873} = 4.8$. Methane $S_{873} = 56.6$.
(*b*) −26 cal/degree.

25. (*a*) From the data of the preceding problem calculate ΔC_p for the reaction

C (graphite) + 2 H_2 (*g*) → CH_4 (*g*)

(*b*) Find an equation expressing ΔH as a function of temperature. ΔH_{298} for this reaction is $-18{,}062$ cal. What is the value of ΔH_0?

(*c*) Calculate ΔH for the reaction at 873° K.

Ans. (*a*) $\Delta C_p = -10.54 + 0.00872\,T + 0.00000067\,T^2$

(*b*) $\Delta H = \Delta H_0 - 10.54\,T + 0.00436\,T^2 + 0.00000022\,T^3$

$\Delta H_0 = -15{,}313$

(*c*) $\Delta H_{873} = -21{,}045$.

26. (*a*) Using the equation for ΔH and the value of ΔH_0 from the preceding problem, give an equation expressing ΔF^0 as a function of temperature. $\Delta F^0_{298} = -11{,}994$ cal. What is the value of I?

(*b*) Calculate ΔF^0_{873} and compare with the value obtained from entropy data on p. 528.

(*c*) Calculate K_p for the reaction C (graphite) + 2 H_2 (*g*) = CH_4 (*g*) at 873° from the free energy value of (*b*). Compare with the values derived by other methods on pp. 528 and 530.

Ans. (*a*) $\Delta F^0 = -15{,}313 + 10.54\,T \ln T - 0.00436\,T^2 - 0.00000011\,T^3 + IT$

$I = -47.6$.

(*b*) $\Delta F^0_{873} = +1090$.

(*c*) K_p at 873 = 0.53.

27. Using the values of ΔH_{873} and ΔF^0_{873} obtained from problems 25 and 26 respectively, calculate ΔS_{873} for the formation of methane from hydrogen and graphite.

Ans. -25.4 cal/degree.

28. Calculate the equilibrium constant for the following reaction at 25°.

$$6\ C\ (\text{graphite}) + 3\ H_2\ (g) = C_6H_6\ (l) \qquad \Delta H_{298} = 11{,}700$$

having given from specific-heat measurements down to absolute zero that, $S_{\text{graphite}} = 1.3$, $S_{C_6H_6(l)} = 41.9$ and $S_{H_2} = 31.2$ at 25°.

29. In the reaction

$$\tfrac{1}{2}\ N_2 + \tfrac{1}{2}\ O_2 = NO$$

(*a*) $\Delta H_{298} = 21{,}605$. Calculate K_p at 298° K. from Nernst's constants.

(*b*) $\Delta F^0_{298} = 20{,}850$. Calculate K_p at 298° K.

Ans. (*a*) 10^{-15}. (*b*) 2×10^{-15}.

30. Estimate with the help of Nernst's constants the equilibrium constant for the following reaction at 25° C.

$$3\ H_2\ (g) + 6\ C\ (\text{graphite}) = C_6H_6\ (g) \qquad \Delta H = 19{,}000.$$

31. From the following table of densities at 25°, find by the method of intercepts the partial molal volumes of nitric acid and of water in (*a*) 20%; and (*b*) 70% solutions.

%HNO_3	Density 25°	%HNO_3	Density 25°
0	0.9997	60	1.3600
10	1.0523	70	1.4061
20	1.1123	80	1.4439
30	1.1763	90	1.4741
40	1.2417	100	1.5040
50	1.3043		

Ans. (*a*) $\bar{V}_{H_2O} = 0.9984 \times 18.02 = 17.99$ cc.

$\bar{V}_{HNO_3} = 0.5049 \times 63.02 = 31.82$ cc.

32. By plotting the molar volume against the mol fraction of butyric acid, determine the partial molal volumes of butyric acid and formamide in solutions at 25° for which (*a*) $N_2 = 0.20$; (*b*) $N_2 = 0.80$, using the following data:

Mol fraction butyric acid, N_2	Molar volume cc.
0.0	39.79
0.0490	42.21
0.1430	46.12
0.2010	49.01
0.2989	54.05
0.4973	64.35
0.6987	75.19
0.8957	86 38
1.00	92 42

Ans. (*a*) $\overline{V}_2 = 89.5$.
$\overline{V}_1 = 35.8$.

CHAPTER XX

PHOTOCHEMISTRY*

Radiant Energy. Photochemistry involves the study of chemical reactions produced by radiation, usually in the ultra violet or visible region of the spectrum. Light, electrical waves and heat radiations are all forms of radiant energy which differ only in wave-length. The whole spectrum may be divided as shown in the following scale.

DIVISION OF THE SPECTRUM

Type of Radiation	Hertzian Waves	Infra red	Visible	Ultra violet
Wave-length				
Ångströms	$>10^{13} - 10^{7}$	$10^{7} - 8000$	$8000 - 4000$	$4000 - 500$
Centimeters	$>10^{5} - 10^{-1}$	$10^{-1} - 8 \times 10^{-5}$	$8\times10^{-5}-4\times10^{-5}$	$4\times10^{-5}-5\times10^{-6}$

Type of Radiation	X-Rays	γ-Rays	Cosmic Radiations
Wave-length			
Ångströms	$500 - 1$	$1 - 0\ 1$	$0\ 1 - 0\ 01$
Centimeters	$5\times10^{-6}-1\times10^{-8}$	$1\times10^{-8}-1\times10^{-9}$	$1\times10^{-9}-1\times10^{-10}$

The Hertzian or radio waves are generated by electrons oscillating along a wire and they are absorbed by an antenna wire having the proper capacity and inductance.

Infra-red or heat rays are generated and absorbed by the displacement of atoms in molecules. Visible and ultra-violet radiations are absorbed when outer electrons are displaced in molecules and atoms, and are evolved when the electrons return toward their normal positions. The displacement is greater in the case of ultra-violet light. X-rays involve the displacement of inner electrons in atoms; γ-rays involve the displacements of electrons still deeper, in the central part of the atoms. Cosmic rays, studied by Millikan, have very short wave-lengths and are exceedingly penetrating. They appear to be generated in interstellar space.

Of these various radiations we are concerned here chiefly with the visible and ultra-violet regions, because it is here that photochemical reactions are more frequently effected. Infra-red light seems to be

* Additional material on photochemistry will be found in Chapter XXIV on quantum theory.

inactive* and X-rays and cosmic radiation are so penetrating that the chemical change in an ordinary vessel is small. When the outer or valence electrons are displaced by visible or ultra-violet light, however, the molecules become sufficiently activated to react.

Emission and Absorption. When light strikes a substance, a portion of the incident radiation is transmitted, a portion is reflected, and a portion is absorbed. These three possibilities are illustrated by the passage of visible light through glass, the reflection from silvered glass, and absorption by smoked glass.

The relation between the emissive and absorptive powers of different bodies was first clearly enunciated by Kirchhoff in 1859. This law may be stated as follows:— *Light of any given wave-length emitted by a body can also be absorbed by the same body at a lower temperature.* This law, it will be seen, offers a satisfactory explanation of the Fraunhofer lines in the solar spectrum. The sun is surrounded by a gaseous atmosphere, resulting from the vaporization of the elements present in the body of the sun. Each element in the cooler gaseous envelope, according to Kirchhoff's law, absorbs those wave-lengths which it emits at the higher temperature of the sun's center. The resulting dark lines of the solar spectrum have enabled the astronomer to determine the elementary composition of the sun.

If the emissive and absorptive powers of a body are denoted by E and A respectively, then according to Kirchhoff's law,

$$E/A = S, \tag{1}$$

where S is a constant. When absorption is complete, A is unity and $S = E$. Under these conditions the constant S may be defined as the emissivity of a body which absorbs all the incident radiation and reflects none. Such a body is called a perfectly *black body*, or better, a *perfect radiator*. Although the experimental realization of a perfect radiator is impossible, a very close approximation can be obtained by the employment of a hollow blackened sphere, perforated by a small hole to permit the passage of the radiation. When this sphere, sometimes called a *hohlraum*, is heated, practically all the radiation is absorbed by multiple reflections at the inner surface. "It has been found that, where such a black body is not available, or where extreme accuracy is not required, a thin strip of platinum foil coated with ferric oxide and heated electrically proves a satisfactory substitute."

The value of the emissivity constant S is the same for all materials at a given temperature, but the emissive power E decreases when the absorption becomes less than unity, as shown by equation (1).

* Daniels, Chem. Rev., **5**, 39 (1928).

A familiar qualitative illustration of Kirchhoff's law is that afforded by the appearance of a fragment of white chinaware, decorated with a dark pattern, when heated to a high temperature. When cold, the dark parts absorb light, whereas the white parts reflect it. On heating the fragment to redness, the pattern will be reversed, the dark portions of the design appearing bright, and the white portions dark.

It has been shown that the law of Kirchhoff is a necessary consequence of the application of the second law of thermodynamics to the thermal equilibrium within an enclosure whose walls are impervious to heat.

Laws of Radiation. From a study of the experiments of Dulong and Petit on the rate of cooling of different bodies, Stefan discovered in 1879 an empirical relation between the total radiation of a body and its temperature. Later, Boltzmann* derived the same relation thermodynamically and showed that instead of being general, as Stefan supposed, it is strictly applicable only to a perfectly black body. The Stefan-Boltzmann law may be stated as follows: — *The total radiation from a perfect radiator is directly proportional to the fourth power of the absolute temperature.* If the total radiation is denoted by S, we may write,

$$S = CT^4, \tag{2}$$

where C is a constant. This law is tested by measuring the heat radiated from the small opening in a heated vessel and received on a thermopile. The quantity of radiation striking the receiver per second is determined at various temperatures, and C has been found to have the value 5.709×10^{-5} erg, cm.$^{-2}$ sec.$^{-1}$ deg.$^{-4}$.

If the radiation from the sun is considered solely as a temperature effect, its temperature may be calculated by equation (2) expressing the Stefan-Boltzmann law. Employing available data, the temperature of the sun may thus be shown to be 6200° K.

Having considered the total energy radiated by a given source, we now come to the consideration of the distribution of energy throughout the entire spectrum in its relation to temperature. The results of the experiments of Lummer and Pringsheim† on the distribution of energy in the normal spectrum of a black body are represented graphically in Fig. 158. The values of the energy radiated by the source are plotted as ordinates against the corresponding values of the wave-length as abscissas.

These measurements may be made by spreading out with a fluorite prism the total radiation from a perfect radiator. A thermopile is

* Wied. Ann., **22**, 291 (1884).

† Verh. deutsch. phys. Ges., **1**, 230 (1889); **3**, 36 (1901).

then moved along in different parts of the spectrum and the deflections of the galvanometer connected to the thermopile will be proportional to the intensity of radiation falling on the receiver.

It will be observed that the energy corresponding to a definite wave-length increases with the temperature, and that each curve, or isothermal, exhibits a distinct maximum. The position of this maximum is displaced in the direction of decreasing wave-length as the temperature is raised.

In 1893, Wien* discovered the law governing this displacement of the energy maximum with temperature. If λ_{max} denotes the wave-length corresponding to the energy maximum, and T is the absolute temperature of the radiating black body, Wien showed that

$$\lambda_{max} \times T = \text{constant}.$$

Furthermore, Wien found that

$$S_{\lambda\,max} = BT^5, \qquad (3)$$

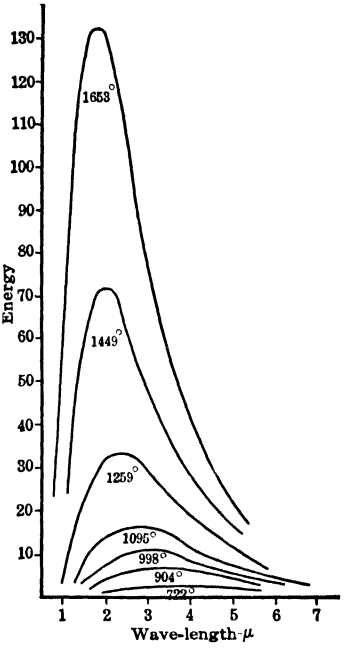


FIG. 158

where $S_{\lambda\,max}$ is the maximum emissivity corresponding to λ_{max}. In general, the emissivity S_λ is the amount of energy radiated per square centimeter per second in a narrow strip of the spectrum corresponding to the mean wave-length λ.

The actual distribution of energy throughout the spectrum resolves itself into the measurement of the energy emitted between two contiguous wave-lengths, λ and $\lambda + d\lambda$. In other words, we actually measure the energy of a very small portion of the spectrum included between two wave-lengths which lie very close together.

The formulas of Rayleigh and Wien have been found to reproduce the experimental values with considerable accuracy. The formula of Rayleigh has the following form,

$$S_\lambda = \frac{CT}{\lambda^4} \cdot e^{-\frac{C'}{\lambda T}}: \qquad (4)$$

while that of Wien may be written thus,

$$S_\lambda = \frac{C}{\lambda^5} \cdot e^{-\frac{C'}{\lambda T}}. \qquad (5)$$

* Wied. Ann., **58**, 662 (1896).

In these two formulas, C and C' are constants, and the other symbols have their usual significance. The formula of Rayleigh holds only in the region of the longer wave-lengths whereas the formula of Wien holds only for short waves. It should be remembered that both these formulas apply only to bodies emitting continuous spectra.

Realizing the limitations of these formulas, Planck,* in 1900, derived a better equation which expressed the experimental facts with remarkable exactness over the whole range of the spectrum. In deriving this equation Planck was led to the arbitrary conclusion that radiation is emitted and absorbed discontinuously in integral multiples of a fundamental unit which he called a quantum ϵ, and that the energy of a quantum is proportional to the frequency of the light. This suggestion led to the *quantum theory*, which has become of very great importance. It will be discussed briefly in Chapter XXIV.

The fundamental equation of the quantum theory is

$$\epsilon = h\nu \tag{6}$$

in which ν is the frequency of the light and h is Planck's constant 6.547×10^{-27} erg-seconds.

Luminescence. When a solid body, a bar of iron for example, is heated to about 500°, it becomes "red hot"; when the temperature is raised still higher, it becomes "white hot," as the wave-lengths of maximum intensity shift toward the shorter end of the spectrum in accordance with Wien's displacement law. It is possible, however, to produce light by other agencies than heat, and the radiation thus produced is called *luminescence* or sometimes "cold light." In all cases the emission of visible light may be attributed to the return of an outer electron toward its normal position after being displaced by kinetic bombardment of atoms and molecules, or by chemical or electrical or other forms of energy.

Chemiluminescence is a phenomenon which accompanies certain chemical reactions. Thus Evans and Dufford† have shown that the oxidation of ethereal solutions of magnesium *p*-bromphenyl bromide gives rise to marked chemiluminescence, the greenish-blue glow which accompanies the exposure of the solution to air being visible in day light. The oxidation of certain decaying wood, of luciferin in fireflies and of yellow phosphorus are further examples.

Thermoluminescence is the name given to luminescence stimulated by heat, but at a temperature considerably lower than that required for

* Planck, "Wärmestrahlung."

† Evans and Dufford, J. Am. Chem. Soc., **45**, 278 (1923).

pure temperature radiation. In such cases a preliminary exposure to light is often necessary.

Fluorescence involves the emission, by an illuminated medium, of light of a wave-length different from that of the incident radiation.

In general, the wave-length of the transformed radiation is greater than that of the incident radiation. This relation, to which numerous exceptions have been discovered, was first enunciated by Stokes. When the incident radiation is cut off, fluorescence ceases.

Among the numerous substances which are known to exhibit the phenomenon of fluorescence may be mentioned fluorite (from which the phenomenon derived its name), uranium glass, petroleum, solutions of organic dyestuffs, and quinine sulphate. The vapors of sodium, mercury, and iodine have been found by Wood to fluoresce brilliantly.

There are also many substances known which continue to emit light for some time after the external light-stimulus is removed. This phenomenon is termed *phosphorescence*, and appears to be governed by Stokes' law for fluorescence.

The sulphides of the alkaline earths may be mentioned as examples of phosphorescent substances. The investigations of Lenard and Urbain have revealed the interesting fact that the presence of a trace of one of the heavy metals greatly intensifies the light emitted by a phosphorescent substance. Usually impurities, in the form of mixed crystals, are necessary for phosphorescence.

When certain crystals, such as those of cane sugar, are either crushed, or simply rubbed together, flashes of light are emitted. This phenomenon is known as *triboluminescence.*

Cathodo- and *radioluminescence* may be considered as subdivisions of the more inclusive term, *electroluminescence.* It will be shown in the following chapter that the residual gas in a vacuum tube is rendered luminous by the passage of the electric discharge, and also that certain minerals become luminescent when placed in the path of the cathode rays. These may be taken as examples of cathodoluminescence. The luminosity of a screen coated with crystals of zinc sulphide, when subjected to the action of the α-particles shot out from a radioactive substance, will be mentioned in a subsequent chapter. This is clearly an instance of radioluminescence.

Absorption and Reflection. After discussing the emission of light it is necessary to consider the laws which govern absorption and reflection. *Lambert's law* of absorption was given on p. 102. According to this law

$$I = I_0 e^{-kl} \qquad (7)$$

where I_0 is the intensity of light striking the absorbing medium, I is the intensity after passing through the distance l, and k is a constant characteristic of the absorbing medium and the wave-length.

In the case of solutions the absorption of light depends not only on the thickness but also on the concentration. According to *Beer's law*, if the thickness of the solution is maintained constant, the absorption of light at different concentrations of the same solute dissolved in the same solvent is an exponential function of the concentration. Then

$$I = I_0 e^{-k'lc} \tag{8}$$

where c is the concentration of the absorbing material and k' is a constant which is characteristic of the dissolved material and the wave-length. The law does not apply if the character of the dissolved material changes with dilution, as for example when the extent of hydration or ionization changes in such a way as to alter the color.

When the light is composed of different wave-lengths, as in white light, different constants are involved and the total effect is quite complex. A substance appears colored because part of the light is absorbed. For example, a solution of copper ions appears blue because, when white light is passed through it, the red and yellow light is absorbed and only the blue is transmitted to the eye. According to present views, visible or ultra-violet light is absorbed by the displacement of electrons in molecules (or atoms or ions), and if a displacement of just the right energy can be effected by a given wave-length, then that light will be absorbed.

The difference between the intensity of the original light and the intensity at thickness l is a measure of the amount of light absorbed, A. Then

$$A = I_0 - I = I_0(1 - e^{-k'cl}). \tag{9}$$

The amount of light reflected at a surface, between two different media, depends on the ratio, μ, of their refractive indices and on the angle of incidence. When monochromatic light strikes the surface perpendicularly, the intensity of the reflected light I_r is related to the incident intensity I_0, according to Fresnel's law by the equation

$$I_r = \left(\frac{\mu - 1}{\mu + 1}\right)^2 I_0. \tag{10}$$

With silver and other metals the refractive index is very large and reflection is practically complete. Even with a substance like glass or quartz the reflection amounts to a few per cent and must be considered in accurate photochemical work. The light passing into a reaction chamber, for example, is given by the expression $I_0 - I_r$.

Laws of Photochemistry. The first law of photochemistry was enunciated by Grotthuss in 1818. It seems obvious that *only those rays of light which are absorbed can produce chemical change.* It does not follow, however, that chemical action *must* accompany the absorption of light. According to present views, visible or ultra-violet light is absorbed by the displacement of electrons in molecules (or atoms or ions) and these energy-rich molecules may decompose or react with other molecules. When the conditions are not favorable for such a reaction, the molecules may emit their energy as fluorescence or they may simply produce more violent collisions with other molecules and give up their energy as heat. In fact, absorbed radiation is usually converted into heat, the conditions favorable to photochemical reactions being comparatively rare.

The Einstein law of photochemical equivalence* has become the guiding principle in the theoretical interpretation of photochemical reactions. According to this law, *in the primary photochemical process each molecule is activated by the absorption of* 1 *quantum of radiation.*

In this simple, primary process, then, we should find that the number of molecules activated is exactly equivalent to the number of quanta absorbed, and for a gram-molecule of 6.06×10^{23} molecules there should be 6.06×10^{23} quanta absorbed. This "gram-molecule" of quanta has been called the "einstein," just as a gram-equivalent of electrons (6.06×10^{23} electrons or 96,500 coulombs) is called the faraday.

It must be strongly emphasized that this Einstein relation is frequently masked by secondary reactions and complicating circumstances which prevent a simple 1 to 1 relationship between the number of quanta absorbed and the number of molecules of *final* products in the reaction. In fact, the 1 to 1 relationship is found so infrequently that the validity of the law has been seriously questioned. However, as the experimental technique is improved and as the secondary reactions are separated from the primary process, it is found that the law is essentially correct. Most investigators are inclined to accept the law and to look for the complicating circumstances which are peculiar to each particular reaction. Sometimes the activation process is followed by a simple stoichiometric reaction which gives a *quantum efficiency* of some simple number, such as 2 molecules per quantum; or, by a series of repeated reactions gives rise to a chain reaction. On the other hand, the activated molecules may be partially deactivated by collisions or by fluorescence, or they may recombine so as to give

* Einstein, Ann. Physik (**4**) **37**, 832 (1912); Verh. deut. physik. Ges., **18**, 315 (1916).

small quantum efficiencies. The quantum efficiencies of a few typical reactions are recorded in the following table.

QUANTUM EFFICIENCY OF PHOTOCHEMICAL REACTIONS

Reaction	Molecules per Quantum
$Br_2 + C_6H_{12} = C_6H_{11}Br + HBr$	1 Br_2
$Cl_2 + 2\ CCl_3Br = 2\ CCl_4 + Br_2$	1 Cl_2
$2\ HI = H_2 + I_2$	2.0 HI
$H_2C_2O_4 (+ UO_2SO_4) = H_2O + CO_2 + CO$	0 57 $H_2C_2O_4$
$2\ O_3 = 3\ O_2$	0.28 O_3
$H_2 + Cl_2 = 2\ HCl$	1.4×10^6 HCl
$CO + Cl_2 = COCl_2$	$2\ 7 \times 10^3$ $COCl_2$

It will be remembered that the energy of one quantum ϵ is proportional to the frequency ν of the light. Multiplying equation (6) by the Avogadro number N, we have

$$N\epsilon = U = Nh\nu, \tag{11}$$

where U is the energy associated with one einstein of radiation and h is Planck's constant having a value of 6.547×10^{-27} erg-second. Since ν is a number divided by time and N is a number, $Nh\nu$ has the dimensions of energy (ergs or calories). The energy associated with quanta of typical wave-lengths is given in the following table.

ENERGY OF DIFFERENT RADIATIONS

Wave-length Å	Approximate Color	$h\nu$ (ergs)	U (cal.)
10,000	Short infra red	1.965×10^{-12}	28,450
7,000	Red	2.81×10^{-12}	40,700
6,200	Orange	3.17×10^{-12}	45,900
5,800	Yellow	3.39×10^{-12}	49,070
5,300	Green	3.71×10^{-12}	53,800
4,700	Blue	x	y
4,200	Violet	4.68×10^{-12}	67,760
3,000	Ultra violet	6.55×10^{-12}	94,840
2,000	Ultra violet	9.83×10^{-12}	142,300
300	X-Rays	6.55×10^{-11}	948,400

The frequency of radiation ν is calculated by dividing the wave-length of light in cm. into the velocity of light, 3×10^{10} cm. per sec. For example, light of 3000 Å, or 300 $m\mu$, or 3×10^{-5} cm., has a frequency of $\frac{3 \times 10^{10}}{3 \times 10^{-5}} = 1 \times 10^{15}$ per sec.

Experimental Technique. In quantitative photochemical investigations it is best to use light of a narrow range of wave-lengths and of measured intensity. The photochemical reactions are influenced by both intensity and wave-length, and it is necessary to separate the two factors.

The intensity of radiation is measured with a thermopile, which consists of a series of junctions of unlike metals, such as bismuth and silver, connected to a galvanometer. Alternate junctions are heated by exposure to the radiation and the galvanometer deflections are proportional to the intensity of radiation. The junctions are covered with blackened metal strips of very low heat capacity, which convert radiation of all wave-lengths directly into heat. The galvanometer readings may be converted into ergs of radiation per second per square millimeter striking the thermopile, by calibrating with a standard carbon filament lamp from the U. S. Bureau of Standards.

The light can be restricted to a narrow range of wave-lengths with the help of properly chosen filters which absorb the undesired wave-lengths. The separation may be effected still better by refraction through a prism in a monochromator; the best results are obtained with a source of light like a mercury vapor lamp which gives a discontinuous spectrum. Under these conditions a single line may be isolated for the photochemical reaction. The intensity obtainable with a monochromator is very low, and it is necessary to use capillary arcs or other very intense sources of light, and to employ prisms and lenses of large dimensions in order to obtain sufficient intensity for a measurable photochemical reaction. The reacting system is placed in glass or quartz vessels provided with clear, polished windows and the light is usually passed through the cell onto the thermopile. The actual energy absorbed in the reacting system is measured by subtracting these readings from those obtained with the thermopile at the front of the cell, after small corrections for reflection.

Failure to control the wave-length and intensity may lead to erroneous conclusions. For example, when a certain reaction is exposed to sunlight through a red filter it may proceed faster than when exposed through a blue filter. But red light is present in sunlight in much greater intensity than the blue and one cannot conclude that the red light is more effective than the blue light. As another example, one may cite the action of the mercury vapor lamp in producing ozone from oxygen. Ozone is synthesized by the short ultra violet and decomposed by longer ultra violet (2800 Å). The actual yield of ozone depends then on the ratio of the intensities in these two regions, and this ratio depends on accidental conditions such as the age and the

rate of cooling of the lamp. Experimental checks under uncontrolled conditions of this type are not to be expected. Obviously the Einstein equivalence law cannot be tested unless monochromatic light is used, because the thermopile measures the total effect of all the radiations while the absorption process may be restricted to only a portion of the wave-lengths.

Actinometers. The intensity of light available for photochemical reactions is measured most accurately with a thermopile, but it may be measured by the amount of photochemical reaction produced in an actinometer.

One of the earliest reactions used for this purpose was the combination of hydrogen and chlorine in the presence of light to give hydrochloric acid. Bunsen and Roscoe in 1857 used such an actinometer. The gases were produced in equimolecular proportions by electrolyzing hydrochloric acid, and the shrinkage in volume on illumination was caused by the photochemical formation of hydrochloric acid and its solution in water. The rate of decrease in volume is proportional to the intensity of the light, and the actinometer is sensitive to small amounts of visible or ultra-violet light. If the light is intense, an explosion may occur.

In the mercuric oxalate actinometer, a mixture of mercuric chloride and oxalic acid is exposed to ultra-violet light and the amount of evolution of carbon monoxide and carbon dioxide is proportional to the intensity of the light. Both these actinometers involve chain reactions in which the chemical effect of the light is greatly magnified.

The best actinometer is that employing uranyl oxalate. The results of the early investigators did not check, but the recent research of Leighton and Forbes* constitutes perhaps the most exact photochemical investigation yet described. Although the quantum efficiency changes slightly with the wave-length, it may be assumed that in a solution $M/100$ in UO_2SO_4 and $M/20$ in $H_2C_2O_4$, 0.57 molecule of the oxalic acid is decomposed for each quantum of light absorbed between the wave-lengths 254 and 435 $m\mu$. In other words each mol of oxalic acid decomposed is equivalent to 1.75 einstein, or to 166,000 calories, assuming an average wave-length of 300 $m\mu$.

Kinetics. The kinetics of photochemical reactions are more complicated than the kinetics of thermal reactions because more variables are involved. The intensity of light and the size and shape of the vessel may affect the rate of a photochemical reaction. A photochemical reaction may be accompanied by a thermal reaction, identical with the photochemical reaction, or opposite to it, or entirely different

* J. Am. Chem. Soc., **52**, 3139 (1930).

in character. A photochemical reaction may produce a catalyst which then causes a thermal reaction to proceed at a measurable rate. Sometimes an *induction period* is necessary while a sufficient quantity of catalyst is being accumulated to make the reaction proceed with a measurable velocity. Again a thermal reaction once started may continue after the illumination is stopped, giving an *after-effect.* The energy available in a photochemical reaction is much greater than in the thermal reaction, and this fact often changes the character of the reaction. For example, the thermal dissociation of hydriodic acid at 450° is bimolecular ($2\,HI = H_2 + I_2$), but the photochemical reaction is unimolecular ($HI = H + I$) and involves the extra energy required to produce free atoms.

Not only second-order and first-order reactions, but zero-order reactions, also, are found in photochemistry. A zero-order reaction is one in which the rate is entirely independent of the concentration. For example, if the concentration is high and the light intensity is weak, the light intensity may be the limiting factor in the reaction rate and the concentration may be without influence on the rate.

If the reaction cell is shallow, the absorption of light is slight, so that practically all parts of the reacting system have about the same illumination, and stirring becomes unimportant. If, on the other hand, the light is largely absorbed in the first portion of the reacting system, the extent of the reaction will vary with the depth, and vigorous stirring may be necessary to give uniform and reproducible conditions.

If light causes a reaction in one direction, giving a zero-order reaction, and a thermal reaction occurs in the opposite direction proportional to the concentration of the photochemical product, a stationary state will eventually be produced in which the two rates are exactly equal. The situation is described mathematically by the following equation:

$$\frac{dx}{dt} = k_{\text{photo}} I - k_{\text{thermal}}\, x \tag{12}$$

where k_{photo} and k_{thermal} are the specific reaction rates of the photochemical and thermal reactions and x is the amount of material produced by the photochemical reaction. At equilibrium

$$k_{\text{photo}} I = k_{\text{thermal}}\, x, \quad \text{and} \quad x = \frac{k_{\text{photo}} I}{k_{\text{thermal}}}. \tag{13}$$

The concentration of material in the stationary state changes with the intensity of the light. An example of this type of reaction is the photopolymerization of anthracene, dissolved in xylene. In the presence of ultra-violet light this substance forms dianthracene which has twice

the molecular weight of anthracene, but in the dark the dianthracene is depolymerized, giving the original anthracene.

The low temperature coefficient is one of the characteristic features of a photochemical reaction. Whereas a thermal reaction at ordinary temperatures ordinarily doubles or trebles its rate with a rise in temperature of ten degrees, a photochemical reaction usually increases its rate only about 10 per cent or less. Thermal reactions acquire their energy from the particularly violent collisions between molecules in the reacting system, and the number of these collisions is greatly increased by a rise in temperature. Photochemical reactions, however, acquire their energy from outside the system. The temperature of the reaction system then has no influence on the radiation emitted by the external radiator. The primary photochemical process involving the absorption of quanta, to which Einstein's law applies, has a very small temperature coefficient but the thermal reactions which so frequently accompany the photochemical reactions contribute to give a temperature effect.

Chain Reactions. The experimental determination of the quantum efficiency constitutes an excellent method for studying chain reactions (p. 355). If several molecules of products are produced for each quantum of light absorbed the reaction is obviously a chain reaction, in which the products of the reaction return their energy to activate more molecules.

The photo-combination of hydrogen and chlorine is a classical example of such a reaction, about a million molecules reacting for each quantum absorbed. Each molecule of hydrochloric acid formed contributes sufficient energy to cause more molecules to react (p. 355). Often the measurement of the number of molecules per quantum constitutes the only method available for detecting the existence of a chain.

An interesting case is that of the photo-bromination of cinnamic acid.* When the carbon tetrachloride solution of cinnamic acid and bromine contains 0.013 mol of bromine per liter, 11 molecules of bromine react for each quantum absorbed, the energy-rich molecules of brom-cinnamic acid passing over their energy to more molecules of bromine. The chain would be longer except for the fact that the molecules lose their energy by collisions with the molecules of the solvent. When the solution contains only 0.002 mol of bromine per liter, 2.3 molecules react for each quantum absorbed. The energy-rich molecules of products have a greater chance in the dilute solution to dissipate their energy to the solvent because they travel

* Forthcoming publication.

farther before colliding with another bromine molecule. At infinite dilution, in this case, the chain should be completely eliminated and one molecule of brom-cinnamic acid should be produced for each quantum absorbed. In accordance with this hypothesis it is found that plotting quantum yield against concentration and extrapolating to infinite dilution of bromine the yield is actually one molecule per quantum, in agreement with the Einstein law.

Photosensitization. Very often the molecules which absorb the light take part in the photochemical reaction only in an indirect manner and act merely as carriers of energy. One of the outstanding examples is that of mercury vapor, activated by the absorption of ultra-violet light of 2536.7 Å which is emitted by a mercury vapor lamp. The energy corresponding to this radiation is very large (112,000 calories), and it is more than the 101,000 calories necessary to dissociate hydrogen molecules. When mercury vapor is mixed with hydrogen and exposed to light from a mercury vapor lamp, the chief reactions may be represented by the following equations, where Hg* represents an activated mercury atom:

$$\mathrm{Hg} + h\nu = \mathrm{Hg}^*.$$
$$\mathrm{Hg}^* + \mathrm{H_2} = \mathrm{Hg} + 2\,\mathrm{H}.$$

The mercury acts as a photosensitizer, and the hydrogen atoms readily reduce metallic oxides, nitrous oxide, ethylene, carbon monoxide, and other materials. The excited mercury atoms decompose not only hydrogen but ammonia and many different organic compounds.†

In another reaction, chlorine absorbs light and acquires sufficient energy to decompose ozone.‡

Photography. If silver chloride or bromide is mixed with gelatine and given a very brief exposure to light, no change can be detected, but when it is immersed in a solution of a mild reducing agent, such for example as pyrogallic acid, the parts which have been exposed to light are developed; that is, they are reduced to metallic silver much more rapidly than the unexposed parts. The photographic plate consists of a large number of minute grains of crystalline silver halide; some of these grains are completely reduced by the developer to black metallic silver and others are unaffected. Apparently it is necessary for a quantum of energy to strike a sensitive spot in the crystal lattice in order that the silver halide may be reduced to give a nucleus of silver which then spreads on further reduction to include the whole grain. These sensitive spots seem to be identified with minute im-

† Taylor, "Treatise on Physical Chemistry," pp. 1480–1482.

‡ Weigert, Z. Elektrochem., **14**, 591 (1908); Bonhoeffer, Z. Physik, **13**, 94 (1923).

purities of silver sulphide in the crystal lattice which are particularly responsive to the action of light.

The camera and lens focus the image of the object on the photographic plate; the brightest parts of the image have a greater concentration of quanta and consequently more grains are reduced to silver. The unaffected grains are dissolved out with sodium thiosulphate ("hypo") and the plate is washed and dried. The bright parts of the image become the dark spots on the plate, and the plate is therefore called a negative.

In printing, the plate is placed over a paper coated with silver halide and exposed to the light. The dark spots of silver on the negative absorb the light whereas the unaffected areas permit light to pass through and act on the silver halide, producing a negative of the first negative. This double reversal produces a print in which the dark and light parts agree with the dark and light parts of the original object.

The silver halides respond only to the ultra violet, and the shorter wave-lengths of the visible spectrum, but by mixing in the emulsion certain red dyes, such as dicyanin, the plate becomes sensitive also to red. Such red-sensitive plates are called panchromatic plates and give much better tone values to colored objects. This phenomenon constitutes another example of photosensitization. The red light is less refracted than the blue and much clearer pictures of distant objects are obtained with red-sensitive plates using a color filter which absorbs the blue. This method is extensively used in aerial photography.

Biological Applications of Photochemistry. The most important photochemical reaction in the world is the union of carbon dioxide and water in plants through the agency of sunlight and chlorophyll. Chlorophyll is a complex organic compound containing magnesium, which gives to plants their green color. It absorbs both red and blue light and the activated chlorophyll thus formed is responsible for the production of the starting material of all plant growth from carbon dioxide and water. It is possible that sometime a more efficient substance than chlorophyll may be found for effecting the photochemical combination of carbon dioxide and water, and it is conceivable also that the photosynthesis may be accomplished sometime through direct reactions without the agency of the living plant.

The normal deposition of calcium in bones may be effected either by some material present in cod-liver oil, or by a photosynthetic product, produced when ergosterol is radiated with ultra-violet light shorter in wave-length than 3130 Å. The effective material is known as vitamin

D. Rickets, a disease due to the lack of this vitamin, may be prevented or cured by direct radiation of the patient or, as Steenbock* discovered, by radiation of food or oils. In all cases the photochemical reaction involves ergosterol, and the minimum number of quanta necessary to prevent rickets in a rat has been measured quantitatively.†

A new application of photochemistry has recently appeared in the field of genetics. Muller and others have established the fact that mutations, leading to new species, can be produced in plants and insects by radiation with X-rays. Apparently the cells which are responsible for hereditary influence can sometimes be altered by penetrating X-rays. These cells cannot be affected by mechanical methods without destroying the cells, but occasionally they can be influenced without injury by a collision with a quantum of X-rays. Collisions between quanta of X-rays and effective parts of the cells are very rare and can be detected only by the extraordinary magnification occurring in the growth of an organism. It has been suggested that the naturally occurring mutations which are responsible for the spontaneous origin of species and biological evolution are produced by cosmic radiation and γ-rays from traces of radioactive material both of which are similar to X-rays.‡

Another photochemical phenomenon in biology recently reported is that of mitogenetic rays. Evidence is offered to show that certain rapidly growing organisms in the presence of oxygen emit ultra-violet light, so feeble that it can scarcely be detected, but that it apparently accelerates the growth of certain other organisms.§

REFERENCES

Treatise on Physical Chemistry, Chapter XVIII. Taylor.
Photochemical Processes. Kistiakowsky.
J. Phys. Chem., **32**, 481 (1928) Committee on Photochemistry, National Research Council.
J. Phys. Chem., **34**, 2049 (1930). Taylor.
Symposium on Photochemistry. Trans. Faraday Soc. (1931).
Chemical Action of Ultraviolet Rays. Ellis and Wells.
Photochemie. Plotnikow.
Photosynthesis. Spoehr.
Photochemistry. D. W. G. Style.
Experimental Physical Chemistry, Chapters XVII and XXXIV. Daniels, Mathews and Williams.

* J. Biol. Chem., **63**, 25 (1925).
† J. Am. Chem. Soc., **50**, 923, 2573 (1928).
‡ Am. Naturalist, **64**, 220 (1930).
§ Hollaender and Schoeffel, Quart. Rev. Biol., **6**, 215 (1931), give a brief review of this subject.

PROBLEMS

1. A hollow sphere, with an opening of one square centimeter area is heated electrically to 527° C.

(*a*) What is the total energy emitted per second?

(*b*) How much energy is emitted per second if the temperature is 1600° K.?

(*c*) How long would it take the radiant energy emitted at each of these temperatures to melt 10 grams of ice?

2. Derive $I = I_0 e^{-kl}$ and $k = \frac{2.303}{l} \log \frac{I_0}{I}$, from $-\frac{dI}{dl} \propto I$.

3. Acetone vapor in a cell 10 cm. deep absorbed 90 per cent of the light of 313 $m\mu$ which entered the vapor. (*a*) What per cent of light will be absorbed in passing through 2 cm. of the vapor? (*b*) How deep should the absorbing layer be to absorb 50 per cent of the light?

4. A certain red solution 1.5 cm. in thickness absorbs 10 per cent of the blue light passing through. (*a*) What per cent will be absorbed by a layer 6.0 cm. in thickness? (*b*) By a layer 60 cm. in thickness. (*c*) What thickness is necessary to absorb 99 per cent?

5. A colorimetric standard of concentration c was compared in a colorimeter with an unknown solution of concentration x. The colors matched when the length of the column of standard solution was l and that of the unknown solution was y. Express x in terms of known and measurable quantities.

6. A rectangular quartz cell with the windows perpendicular to the beam of light is used to contain an aqueous solution in a quantitative photochemical research. The index of refraction of the quartz is 1.5 and that of the solution is 1.357 for the wave-length used.

Calculate the per cent loss of light by reflection for (*a*) the empty cell; (*b*) the cell containing the solution. *Ans.* (*a*) 4 per cent at each surface.

7. (*a*) Calculate x in the table on p. 546.

(*b*) Calculate y in the table on p. 546.

8. (*a*) What is the energy per quantum ϵ of X-rays of 1×10^{-8} cm. wave-length?

(*b*) How many calories are there in one einstein (6.06×10^{23} quanta) of this radiation?

9. (*a*) What is the energy per quantum, ϵ, of violet light having a wave-length of 400 $m\mu$?

(*b*) How many calories are there in one einstein (6.06×10^{23} quanta) of this radiation?

10. What wave-length in Ångströms corresponds to 24,700 calories? (The energy of activation of nitrogen pentoxide is 24,700 calories.)

11. In an oxalic acid-uranyl sulphate actinometer, 0.6 molecule of oxalic acid is decomposed per quantum of energy absorbed at a wave-length of 254 $m\mu$.

(*a*) How many quanta are absorbed per gram of oxalic acid decomposed?

(*b*) How many ergs are required to decompose one milligram of oxalic acid?

12. Assume that the energy of all wave-lengths between 254 $m\mu$ and 435 $m\mu$ is completely absorbed in an actinometer containing 20 cc. of $M/20$ oxalic acid which is $M/100$ with respect to uranyl sulphate. After two hours exposure to ultra-violet light, the solution required 34 cc. of $KMnO_4$ solution to titrate the undecomposed oxalic acid. The same volume, 20 cc., of unilluminated solution required 40 cc. of the $KMnO_4$ solution. If the average energy of the quanta in this range may be taken as corresponding to a wave-length of 350 $m\mu$, how many ergs were absorbed per second in this experiment? *Ans.* 124,000 ergs.

13. If the actinometer in the preceding problem had an absorbing surface of 3 square centimeters and was 15 centimeters from the mercury arc producing the light, what is the total energy in joules per second emitted as ultra-violet light by the arc (assuming that the arc emits with equal intensity in all directions)?

Ans. 11.7 joules/sec.

14. A sample of gaseous acetone is irradiated with monochromatic light of a wave-length of 3130 Å. Light of this wave-length decomposes the acetone according to the equation

$$(CH_3)_2CO + h\nu \rightarrow C_2H_6 + CO.$$

The reaction cell used has a volume of 59 cc. The acetone vapor absorbs 91.5 per cent of the incident energy. During the experiment the following data are obtained:

Temperature of Reaction	= 56.7° C.
Initial Pressure	= 766.3 mm.
Final Pressure	= 783.2 mm.
Time of Radiation	= 7 hours
Incident Energy	= 48,100 ergs per second

How many molecules are decomposed per quantum of absorbed energy?

Ans. 0.166 molecule.

15. Two molecules of nitrosyl chloride are decomposed according to the reaction

$$2\,NOCl \rightarrow 2\,NO + Cl_2$$

per quantum of light absorbed in the region from 3650 Å to 6350 Å. Suggest a possible mechanism for the decomposition which is in accord with this experimental fact.

16. The photo polymerization of anthracene reaches a stationary state due to the thermal decomposition of the dianthracene. For the photo reaction the temperature coefficient, r is 1.1 and for the thermal reaction r is 2.8 where r is defined as $\frac{k_{t+10}}{k_t}$.

Calculate the effect of a 10° rise in temperature upon the amount of dianthracene formed when the photo-stationary state is reached.

Ans. 60.7 per cent decrease.

17. When ergosterol is irradiated with ultra-violet light below 3000 Å, vitamin D, the anti-rachitic vitamin, is produced in proportion to the number of quanta absorbed. When irradiated ergosterol was included in a diet otherwise devoid of vitamin D, it was found that absorbed radiant energy of about 750 ergs was necessary to prevent rickets in a rat when fed over a period of two weeks. The light used had a wave-length of 265 $m\mu$.

(*a*) How many quanta are necessary to give 750 ergs?

(*b*) Assuming that Einstein's law applies to this reaction, how many molecules of vitamin D per day are necessary to prevent rickets in a rat?

(*c*) If vitamin D has a molecular weight of this same order of magnitude as ergosterol (382) how many grams of vitamin D per day are necessary to prevent rickets in a rat?

CHAPTER XXI

THE ELECTRICAL THEORY OF MATTER

Conduction of Electricity through Gases. Under ordinary conditions, gases are practically non-conductors of electricity, but when a sufficiently great difference of potential is established between two points within a gas, an electric discharge takes place between the points. The potential necessary to produce such a discharge is quite high, forty thousand volts being required to produce a spark of one centimeter length in air at ordinary pressures. The pressure of the gas has a marked effect upon the character of the discharge and the potential required to produce it. It we make use of a glass vessel similar to that shown in Fig. 159, the effect of pressure on the nature of the discharge may be studied. This apparatus consists of a straight glass tube about 40 centimeters long, into the ends of which platinum electrodes are sealed. It is connected to a vacuum pump and a manometer. If the electrodes are connected with an induction coil, and the pressure within the tube is gradually diminished, the following changes in the character of the discharge are observed. At first, the spark becomes more uniform and then broadens out, assuming a bluish color. When a pressure of about 0.5 millimeter is reached, the negative electrode, or *cathode*, appears to be surrounded by a thin luminous layer and between this and the anode is a series of luminous striations separated by dark regions, the number of which depends on the pressure, the kind of gas, and the dimensions of the vessel.

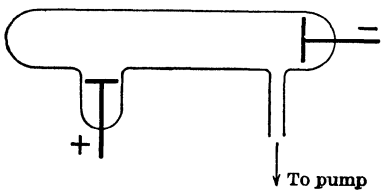


FIG. 159

The current is carried between the electrodes partly by electrons and partly by gas ions. Positive gas ions are produced when molecules have their outer electrons removed, and negative ions are produced when the electrons become attached to other molecules. Gas ions, then, are similar to electrolytic ions, which have been studied in earlier chapters, but they are not governed by stoichiometrical valence numbers, and mercury, for example, can exist with 0, 1, 2, 3, etc., charges. Furthermore, the electrolytic ions are present before the

passage of the electrical current but the gas ions are largely produced by the current itself, the few original electrons and ions acquiring sufficient velocity in the electrical field to produce other ions by dislodging electrons from neutral molecules. The dark spaces in the discharge tube indicate the regions where the electrons are developing sufficient kinetic energy to ionize molecules. Light is produced when ions are discharged and electrons return toward their normal positions.

When the pressure is reduced to about 0.01 millimeter a new phenomenon is observed. The luminous columns disappear and the walls of the tube opposite the cathode become luminescent, the color of the luminescence depending on the nature of the glass. With soda glass the glow is greenish yellow, whereas with lead glass it is bluish. The luminescence is caused by the bombardment of the glass by negative particles projected from the cathode, and is called cathodoluminescence. These cathode rays are now known to be streams of electrons.

Properties of Cathode Rays. The discovery and interpretation of cathode rays by Sir. J. J. Thomson, Sir William Crookes, and others laid a foundation for much of the experimental work which led to rapid developments in our theories of atomic structure. It was found that an opaque object placed in the path of the cathode rays casts a shadow and that the rays travel in straight lines from the cathode. A small paddle wheel was made to revolve by the cathode rays, thus showing that the rays possess mechanical energy. If a concave cathode is used, the rays can be focused on a piece of platinum or other material so as to produce incandescence, thus showing that the rays possess considerable energy which can be converted into heat. Many substances show the phenomenon of cathodoluminescence, including calcite, barium platino-cyanide, willemite, and various kinds of glass.

Although the cathode rays are stopped by opaque objects, they can penetrate very thin sheets of metal and other material. Lenard in 1894 demonstrated the passage of cathode rays through a thin aluminum window in the tube opposite the cathode. Coolidge* has developed a cathode-ray tube which can be used on a large scale for the production of cathode rays, the electrons passing through a considerable distance of air at ordinary pressures. The extent of the penetration depends on the density of the absorbing material and on the applied voltage.

The electrical properties of cathode rays are readily demonstrated by the fact that they are deflected in an electrostatic field toward the

* J. Franklin Inst., 202, 693 and 721 (1926).

positive electrode, thus indicating a negative charge. When a magnetic field is applied at right angles to the rays, they are deflected in the direction which indicates that they are negative charges moving away from the cathode. When the magnetic field is reversed, the direction of deflection is reversed. The actual demonstration that the electrons carry a negative charge was carried out by Perrin.

A modification of Perrin's apparatus, due to Sir J. J. Thomson, is shown in Fig. 160. It consists of a spherical bulb to which is sealed a smaller bulb, and a long side tube. The small bulb contains the

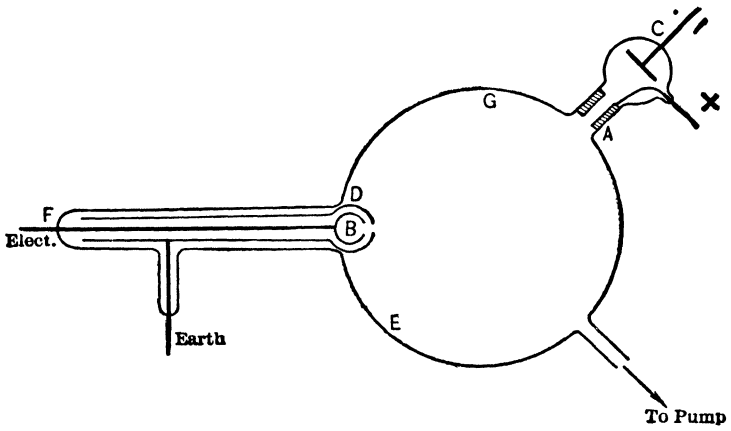


FIG. 160

cathode *C*, and the anode *A*. The anode consists of a tight-fitting brass plug pierced by a central hole of small diameter. The side tube, which is out of the direct range of the cathode rays, contains two coaxial metallic cylinders, insulated from each other, each being perforated with a narrow transverse slit. One of these, *D*, is grounded; *B* is connected with an electrometer by means of the rod *F*. When the tube has been pumped down to the proper pressure for the production of cathode rays, a phosphorescent spot will appear at *E*, directly opposite the cathode *C*. Upon testing *B* for possible electrification by means of the electrometer, it will be found to be uncharged. If the cathode stream is deflected by means of a magnet, so that the rays fall upon *B*, a sudden charging of the electrometer will be observed, proving that *B* is becoming electrified. Upon deflecting the rays still further, so that they are no longer incident upon *B*, the accumulation of the charge will immediately cease. If the electrometer is tested for polarity, it will be found to be negatively charged, thus proving the charge carried by the cathode rays to be negative.

Velocity of the Cathode Particle. Since the cathode rays consist of minute, negatively charged particles which can be deflected by a magnetic and an electrostatic field, it is possible to measure their speed, and to compute the ratio of the mass of a particle to its charge. The special form of tube shown in Fig. 161 was devised for the purpose by Sir J. J. Thomson. It consists of a glass tube about 60 centimeters in length, furnished with a flat circular cathode C, and an anode A, in the form of a cylindrical brass plug about 2.5 centimeters in length,

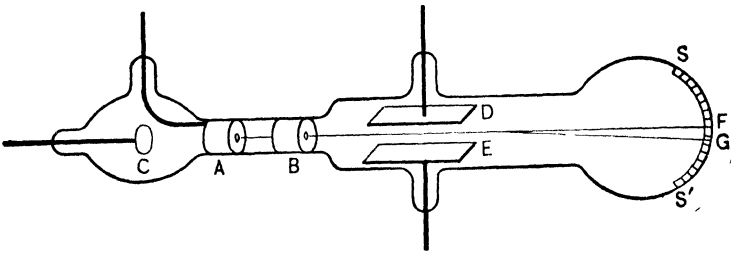


FIG. 161

pierced by a central hole 1 millimeter in diameter. Another brass plug B is placed about 5 centimeters away from A, the two holes being in exactly the same straight line, so that a very narrow bundle of rays may pass along the axis of the tube and fall upon the phosphorescent screen at the opposite end of the tube. Upon this screen is a millimeter scale SS'. Two parallel plates, D and E, are sealed into the tube for the purpose of establishing an electrostatic field. When the tube is connected with an induction coil, or other source of high potential, a phosphorescent spot appears at F. If a strong magnetic field is applied, the lines of force being at right angles to the plane of the diagram, the rays will be deflected vertically, and the spot on the screen will move from F to G. Let H denote the strength of the magnetic field, and let m, e and v represent, respectively, the mass, charge and velocity of a cathode particle. A magnetic field, H, acting at right angles to the line of flight of the cathode particle will exert a force, Hev, which will tend to deflect the particle from a rectilinear path. This force must be equal to the centrifugal force of the moving particle acting outwards along its radius of curvature. Therefore,

$$Hev = \frac{mv^2}{r},$$

or

$$Hr = \frac{mv}{e}. \qquad (1)$$

Since both H and r can be measured, the ratio mv/e can be determined. Now if a difference of potential is established between D and E, and

the lines of force in the electrostatic field have the proper direction, it is possible to alter the strength of the field so as just to counterbalance the effect of the magnetic field, and bring the phosphorescent spot back to F again. Under these conditions, if X denotes the strength of the electrostatic field, we have

$$Xe = Hev,$$

or

$$v = \frac{X}{H}. \tag{2}$$

Since both X and H can be measured, v can be calculated, and, by introducing the value so obtained into equation (1), the ratio m/e can be evaluated. By this method, the value of v was found to be 6×10^9 centimeters per second, at a potential of 10,000 volts, and the mean value of the most trustworthy determinations of the ratio m/e at low velocities was found to be 5.65×10^{-8} gram per electromagnetic unit. At velocities approaching the velocity of light the mass increases in accordance with the theory of relativity.

Charge Carried by the Cathode Particle. Until the value of the charge carried by the cathode particle has been determined, it is clearly impossible to compute its mass. Only a brief outline of the method employed to determine this quantity can be given here. Upon suddenly expanding a volume of saturated water vapor, its temperature is lowered with the simultaneous formation of a cloud, each particle of dust present serving as a nucleus for a fog particle. If sufficient time is allowed for the mist to settle and the vapor to become saturated again, a repetition of the preceding process will result in the formation of less mist, owing to the presence of fewer dust particles. By repeating the operation enough times, the space may be rendered dust free, and then the water vapor may be supercooled without forming a mist. Cathode particles, however, serve as nuclei for the condensation of water vapor, just as the dust particles do, and a determination of the number of drops gives directly the number of cathode particles.

It has been shown by Sir George G. Stokes that if a drop of water of radius r is allowed to fall through a gas of viscosity η, then the velocity with which the drop falls will be given by the equation,

$$v = \frac{2}{9} \cdot \frac{gr^2}{\eta}, \tag{3}$$

where g is the acceleration due to gravity. The viscosity of air at any temperature being known, a cloud can be produced by expansion of water vapor in the presence of cathode particles in an appropriate chamber. The speed v with which the cloud falls can be measured,

and hence r can be calculated by means of equation (3). If m is the total mass of the cloud, and n is the number of drops per cubic centimeter, then

$$m = 4/3\ n\pi r^3 \text{ (density of water = 1).}$$

A simple application of thermodynamics to the adiabatic condensation of the gas enables one to calculate the value of m. Knowing the values of m and r, the number of drops in the cloud, n, which is the same as the number of cathode particles, can be calculated. It is a simple matter to measure the total charge in the expansion chamber, and if this is divided by the total number of charged particles, the charge e carried by a single particle will be obtained.

An ingenious modification of the foregoing method, based upon the fact that when X-rays are passed through air or any other gas some of the molecules are broken up into positively or negatively charged carriers of electricity called ions, has enabled Millikan* to determine the value of e with extreme accuracy. A sketch of the apparatus used by him is shown in the accompanying illustration, Fig. 162. A finely divided spray of oil, or some other liquid, is intro-

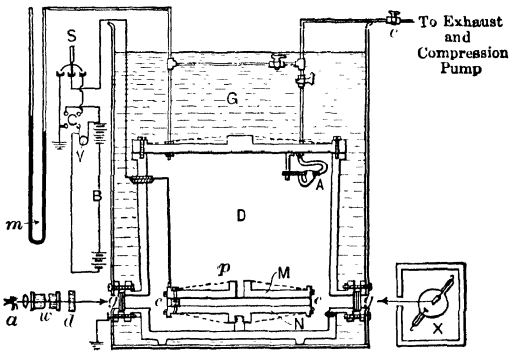


FIG. 162

duced into the chamber D, by means of the atomizer A, until one of the tiny drops eventually finds its way through the aperture p, into the space between the two condenser plates M and N. The hole p is then closed, and the air between the plates is ionized by means of the X-ray tube X. The arc lamp a serves to illuminate the drop, and its motion is observed through a microscope, not shown in the figure. The eye-piece of the microscope is fitted with an engraved glass scale, which enables the observer to measure accurately the motion of the drop. When the drop collides with one of the ions of the air in the condenser chamber, it acquires an electric charge, the sign of which

* Phys. Rev., **39**, 349 (1911); **2**, 143 (1913).

will determine the subsequent direction of its motion with reference to M and N. By means of the switch S the signs of the charges on the two plates can be reversed, thus causing a corresponding reversal of the direction of motion of the drop. By careful adjustment of the difference of potential between the plates, it is possible to keep the drop in the field of view during an entire experiment. Any change in the speed of the drop is an indication of a change in the charge which it carries. Therefore, since the speed with which the drop moves is directly proportional to the magnitude of its charge, it follows that, by measuring the change of speed and comparing it with the speed of the drop when falling under the influence of gravitational attraction alone, the value of the charge carried by the drop can be calculated.

Millikan observed that several electronic charges were quite commonly acquired by a single drop, but in every case the total charge was invariably an exact integral multiple of the elemental charge, e. The value of e given by Millikan as the mean of a large number of determinations is 4.774×10^{-10} electrostatic unit; this result is believed to be in error by less than 0.1 per cent. In the following table are given some of the more recently determined values of e, as found by several observers using different experimental methods.

VALUES OF THE ELEMENTAL ELECTRIC CHARGE, e

Observer	Method	e in e.s.u.
Millikan	Oil or mercury	4.77×10^{-10}
Begeman	Water drops	4.67×10^{-10}
Roux	Sulphur drops	4.17×10^{-10}
Ehrehaft	Metallic dust	4.65×10^{-10}
Rutherford	Counting α-particles	4.65×10^{-10}
Planck	Radiation data	4.69×10^{-10}

Avogadro's Constant. The measurement of the charge on the electron gives the most accurate method for calculating the number of molecules in a gram-molecule, known as Avogadro's constant. In making these calculations it is necessary to use uniform units, and it should be emphasized that the practical unit of electrical charge, the coulomb, is one-tenth of the electromagnetic unit (p. 362) and that a charge expressed in electromagnetic units (e.m.u.) is converted into electrostatic units (e.s.u.) by multiplying by the velocity of light (2.999×10^{10}). Then,

$$\text{charge on electron} = 4.774 \times 10^{-10} \text{ e.s.u.} = 1.592 \times 10^{-20} \text{ e.m.u.}$$
$$= 1.592 \times 10^{-19} \text{ coulomb.} \qquad (4)$$

The ratio of mass to charge, m/e, for the hydrogen ion in electrolysis is found by experiment to be

$$\frac{m}{e} = \frac{1.0078 \text{ gram}}{9{,}650 \text{ e.m.u.}} = 1.044 \times 10^{-4} \tag{5}$$

and the charge of the hydrogen ion is found to be the same as that of the electron, namely 1.592×10^{-20} e.m.u., but opposite in sign.

$$m = 1.044 \times 10^{-4} \times 1.592 \times 10^{-20} = 1.662 \times 10^{-24} \text{ gram.} \tag{6}$$

The mass of 1 mol of hydrogen gas is 2.0156 gram and the number of atoms in a mol of hydrogen is

$$2.0156/1.662 \times 10^{-24} = 1.212 \times 10^{24}. \tag{7}$$

Since each molecule of hydrogen contains 2 atoms, there are then 6.06×10^{23} molecules in a gram-molecule of hydrogen. This is Avogadro's constant. Having established the weight of the hydrogen atom in grams, the weight in grams of the atom of any other element can be calculated from the ratio of its atomic weight to the atomic weight of hydrogen.

The mass of the electron can be determined also. Since e is the same for the hydrogen ion and the electron, and since m/e is 5.65×10^{-8} gram per e.m.u. for the electron and 1.044×10^{-4} for the hydrogen ion, it follows that the mass of the electron is 1/1845 the mass of the hydrogen ion. Since the latter is 1.0078 on the scale of atomic weights (oxygen = 16), the electron must have an "atomic" weight of 0.00054.

Positive Rays. As we have seen, the cathode rays consist of negatively charged particles which are repelled from the cathode of a vacuum tube. These particles, or electrons, under the influence of a high potential, move with an enormous velocity, and, by collision with the atoms of the residual gas within the tube, they remove one or more electrons from these atoms, leaving them with a positive charge. These positively charged atoms are immediately repelled by the anode, and move with high velocity toward the cathode. If a tube with a perforated cathode is used, these positively charged atoms will pass through the perforations into the space behind the cathode, where their properties may be studied. These rays have been called *positive rays* by Sir J. J. Thomson, who has developed an ingenious method for the determination of the individual masses of the positively charged particles by sifting them out into parabolic curves with the help of a magnetic field combined with an electrostatic field.

Aston* has developed an improved apparatus for positive-ray analy-

* Phil. Mag., **38**, 709 (1919).

sis which he calls a "mass spectrograph." This instrument is illustrated diagrammatically in Fig. 163. The positive rays, after reaching the cathode, pass through two narrow parallel slits of special construction S_1S_2, which permit a thin ribbon of rays to pass between the charged plates P_1 and P_2, where they are spread out into an electric spectrum under the influence of the electric field. After emerging

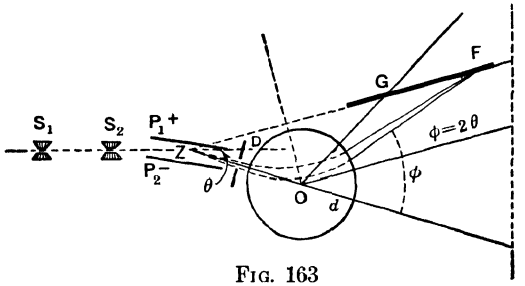


FIG. 163

from the electric field, the rays may be considered as radiating from a virtual source Z, midway through the field on the line S_1S_2. A portion of the emergent rays, deflected through an angle θ from their initial direction, is sorted out by means of a diaphragm D and allowed to pass between the parallel poles of a powerful electromagnet O. The strength of the magnetic field is such that the rays are deflected backward through an angle ϕ, which is more than twice as great as θ. By this means, all the rays having a given ratio of charge to mass are brought to a focus F, where an image is produced on a photographic plate GF. In this way, each class of charged particles will produce its own image at its own particular focus. The resulting series of images is known as a *mass spectrum*. By measuring the displacement of the image produced by a particle of unknown mass, and comparing this with the corresponding displacement of the image produced by a particle whose mass is known, it is possible to determine the mass of the unknown particle. Since in a mass spectrum, all measurements are relative, any known element may be selected as a standard. Obviously, oxygen is taken as the standard, its molecule, its singly charged atom, and its doubly charged atom giving reference lines at 32, 16 and 8, respectively. In a mass spectrum, the displacement with increasing mass is very nearly linear, hence, if the distances from a chosen point of reference are d_1 and d_2, and if m_1 and m_2 are the corresponding masses, it follows that, for given values of d_1 and d_2, the value of the ratio m_1/m_2 will be the same in every experiment. Small amounts of carbon monoxide and carbon dioxide are frequently mixed with the gas under investigation in order to promote the smooth running of the discharge

tube, while traces of hydrocarbons, derived from stop-cock lubricants, are almost invariably present.

A reproduction of the mass spectra of neon and chlorine is given in Fig. 164. The relative masses, taking oxygen as a standard, are indicated by the accompanying numbers. Some of the lines in the neon spectrum correspond to O = 16, C_2 = 24, C_2H_2 = 26 and C_2H_4 or CO = 28, while the two lines produced by neon itself are found to correspond to atomic weights 20.0 and 22.0, rather than to 20.2, the

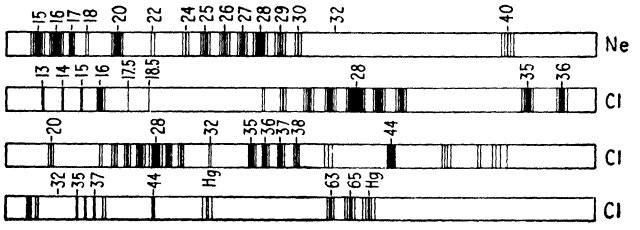


FIG. 164

commonly accepted atomic weight of neon. From this result, Aston concluded that neon is made up of two species of atoms differing in atomic weight by two units. A mixture of nine parts by weight of the lighter atoms with one part by weight of the heavier atoms, would give a gas whose atomic weight would correspond to that assigned to neon in the table of atomic weights.

In like manner, the mass spectrum of chlorine shows some lines at 16, 28 and 44; these are undoubtedly due to the presence of oxygen, carbon monoxide and carbon dioxide, respectively, while the strong lines at 35.0, 36.0, 37.0, and 38.0 indicate the existence of two different species of chlorine atoms, one of which has an atomic weight of 35.0 and the other an atomic weight of 37.0. The other two lines at 36.0 and 38.0 are attributed to the presence of the corresponding hydrogen compounds, HCl^{35} and HCl^{37}.

As will be pointed out in the following chapter, the somewhat revolutionary idea that substances can exist with practically identical chemical and spectroscopic properties and yet differ in atomic weight, was advanced by Soddy and others, several years before Aston furnished direct experimental evidence of the fact. In attempting to find a place for the radio-elements in the periodic table, Soddy found it necessary to assign different elements to the same position in the table, and hence proposed that such elements should be called *isotopes*.

The mass spectrograph has been improved until it is now possible to determine relative atomic weights of isotopes with an error of less than 1 part in 100,000. The relative abundance of the different isotopes

in the positive rays can be determined with an error of about 1 part in 1000 by measuring the intensity of the lines on the photographic plate with a microphotometer. The measurements have been greatly extended with the help of a composite anode of graphite and metallic salts which produces efficient volatilization of the elements and their compounds. With these improvements Aston has succeeded in demonstrating that the isotopic weights are nearly but not quite whole numbers on the O = 16 scale. The following examples are given to show the extent of the deviations from whole numbers. These deviations are attributed to "packing effects" in the atomic nuclei.

Isotope	Weight
H^1	1.00778
He^4	4.00216
O^{16}	15.9980
Cl^{35}	34.983
Cl^{37}	36 980
Hg^{200}	200.016

The table on the opposite page gives the results of determinations by Aston and others of the mass-numbers of isotopes of the elements thus far investigated.

Aston's investigations have thus established the unitary theory of matter and thereby have confirmed, after more than a century of discussion, the essential correctness of the hypothesis of Prout.

Isotopes will be discussed further in later chapters.

X-Rays and Atomic Numbers. Referring back to the experiments on cathode rays, Roentgen in 1895 subjected a stream of electrons to a very high voltage, of about 100,000 volts, and discovered that when the electrons are stopped they emit a very penetrating radiation, which, because of their puzzling characteristics, he called X-rays.

The wave-length of these X-rays was determined later in 1912 by using a crystal as a diffraction grating as described on p. 76. The wave-length depends on the applied voltage and on the anti-cathode or target which is bombarded by the cathode rays. Under controlled conditions the characteristic X-radiation is determined by the elements of which the target is composed, and its penetrating power increases with the atomic weight of the radiating element. With elements whose atomic weights are less than 24, the radiation is too feeble to be easily measured. It will be remembered that most of the properties of the elements such as volume, heats of reaction and normal

MASS-NUMBERS OF ISOTOPES

Element	Atomic No.	Atomic Wt. (1931)	Minimum No. of Isotopes	Mass-numbers of Isotopes in Order of Intensity
H	1	1 008	1	1
He	2	4 00	1	4
Li	3	6.94	2	7, 6
Be	4	9.02	1	9
B	5	10 82	2	11, 10
C	6	12 00	2	12, 13
N	7	14 01	2	14, 15
O	8	16 00	3	16, 18, 17
F	9	19 00	1	19
Ne	10	20 18	3	20, 22, 21
Na	11	23 00	1	23
Mg	12	24 32	3	24, 25, 26
Al	13	26 97	1	27
Si	14	28 06	3	28, 29, 30
P	15	31 02	1	31
S	16	32 06	3	32, 33, 34
Cl	17	35 46	2	35, 37
A	18	39 94	2	40, 36
K	19	39 10	2	39, 41
Ca	20	40 08	2	40, 44
Sc	21	45 10	1	45
Ti	22	47 90	1	48
V	23	50 95	1	51
Cr	24	52 01	3	53, 50, 54
Mn	25	54 93	1	55
Fe	26	55 84	2	56, 54
Co	27	58 94	1	59
Ni	28	58 69	2	58, 60
Cu	29	63 57	2	63, 65
Zn	30	65 38	7	64, 66, 68, 67, 65, 70, 69
Ga	31	69 72	2	69, 71
Ge	32	72 60	8	74, 72, 70, 73, 75, 76, 71, 77
As	33	74 93	1	75
Se	34	79 20	6	80, 78, 76, 82, 77, 74
Br	35	79 92	2	79, 81
Kr	36	82 90	6	84, 86, 82, 83, 80, 78
Rb	37	85 44	2	85, 87
Sr	38	87 63	2	88, 86
Y	39	88 92	1	89
Zr	40	91 22	(4)	90, 94, 92, (96)
Mo	42	96 0	7	98, 96, 95, 92, 94, 100, 97
Ag	47	107 88	2	107, 109
Cd	48	112 41	6	114, 112, 110, 113, 111, 116
In	49	114 80	1	115
Sn	50	118 70	11	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
Sb	51	121 76	2	121, 123
Te	52	127 5	3	128, 130, 126
I	53	126 93	1	127
X	54	130 20	9	129, 132, 131, 134, 136, 130, 128, 126, 124
Cs	55	132 81	1	133
Ba	56	137 36	(2)	138, (136)
La	57	138 90	1	139
Ce	58	140 13	2	140, 142
Pr	59	140 92	1	141
Nd	60	144 27	(4)	142, 144, 146, (145)
W	74	184 0	4	184, 186, 182, 183
Re	75	186 3	2	185, 187
Os	76	190 9	6	192, 190, 189, 188, 186, 187
Hg	80	200 61	6	202, 200, 199, 198, 201, 204
Pb	82	207 22	(6)	208, 207, 206, (209) (203) (204)
Bi	83	209 00	1	209

(Numbers in parentheses are provisional only.)

electrode potentials are periodic functions of the atomic weights, but the penetration of X-rays generated by targets of the different elements is not a periodic function but a linear function of the order in which the elements appear in the periodic table — that is, in the order of the atomic numbers. The X-radiation is nearly independent of

temperature, chemical combination, or other external conditions, thus indicating that the radiation is closely connected with the internal structure of the atoms from which it emanates.

Moseley* performed a classic experiment in 1913 in which he placed different metals as anti-cathodes in an X-ray tube and determined the wave-length of the characteristic X-rays using a crystal plane of sodium chloride for a reflection grating. He found a regular recurrence of certain groups of lines in the X-ray spectra of a number of elements occupying successive positions in the periodic table. These series of lines in the different spectra bore a striking resemblance to each other, both as to their relative positions and their individual intensities. In fact, the only marked difference between the spectra of the different elements was in the wave-lengths of their characteristic lines. With increasing atomic number the entire series of lines constituting the spectra of the elements was found to undergo a gradual shift in the direction of shorter wave-lengths. Furthermore, the elements of higher atomic numbers were found to give two new series of characteristic lines of longer wave-length, and these also underwent a displacement in the direction of shorter wave-lengths as the atomic number of the element increased. These three series of lines have been designated the "K," "L," and "M" series, respectively, and they in turn consist of several lines the prominent doublets of which are designated by α and β.

Moseley discovered that a very simple numerical relationship exists between the frequency of corresponding lines in the X-ray spectra of different elements and their atomic numbers. This relationship may be expressed by the equation

$$\sqrt{\nu} = A(N - b), \tag{8}$$

where ν is the frequency and N the atomic number of the element, and where A and b are constants. From equation (8) it is evident that the square root of the characteristic frequency is a linear function of the atomic number. This law has been found to hold equally well for the K, L and M series, as shown graphically in Fig. 165. It has been shown by Duane,† however, that the square root of the frequency is not quite a linear function of the atomic number N.

In reviewing Moseley's work on X-ray spectra, Soddy‡ says:— "A veritable roll-call of the elements has been made by this method. Thirty-nine elements, with atomic weights between those of alumin-

* Phil. Mag., **26**, 210 (1913); **27**, 703 (1914).

† Phys. Rev., **14**, 516 (1919).

‡ Ann. Reports Progress Chem., p. 278 (1914).

ium and gold, have been examined in this way, and in every case, the lines of the X-ray spectrum have been found to be simply connected with the integer that represents the place assigned to it by chemists in the periodic table."

The atomic number is obtained by starting with the lightest element, hydrogen, as 1 and counting the elements 1, 2, 3, 4, etc., as they occur in

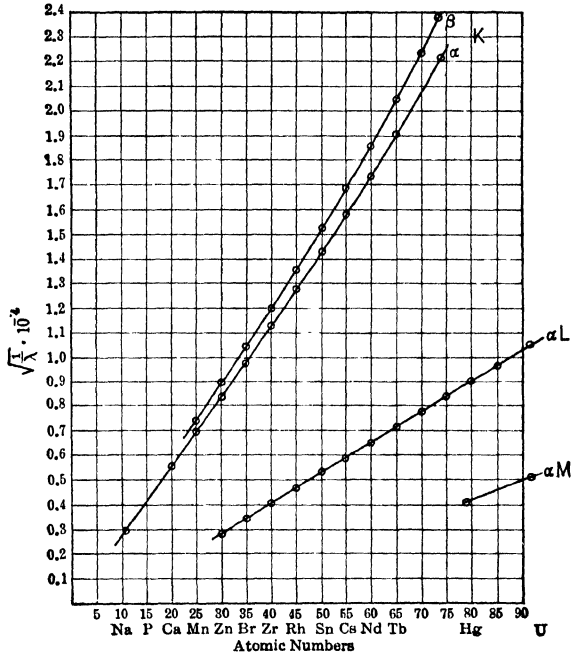


FIG. 165

the periodic table in order of increasing atomic weights. When the atomic weight does not give the exact order which is expected from the chemical properties, as in the case of tellurium and iodine, the order is taken to agree with the position in the periodic table.

As explained in a later chapter, the atomic number is also equal to the positive charge on the center or nucleus of the atom, which in turn is the same as the number of electrons around the nucleus of the uncharged atom.

Since the X-rays from elements lighter than sodium have not been measured, the scale of numbering is extrapolated from sodium to hydrogen. Sodium is the eleventh number in the table and it is given an atomic number of 11. From there on the atomic num-

bers can be calculated directly from the determination of the X-ray wave-length, and the application of equation (8) or interpolation in the graph of Fig. 165. If a new element below sodium should be discovered at some future time, it would be necessary to increase all the atomic numbers by one. Such a discovery is highly improbable.

The arrangement of elements according to their atomic numbers straightened out certain anomalies in the periodic table. Potassium follows argon, nickel follows cobalt, and iodine follows tellurium, in spite of the fact that classification by atomic weights puts them in the reverse order. The existence of isotopes explains why this order is reversed and shows that the atomic number is a more fundamental property than the atomic weight. When Moseley prepared his table of atomic numbers in 1914, there were six gaps corresponding to six missing elements. At least two of these have been discovered since. Before the discovery of Moseley's relation there was doubt concerning the number of rare earth elements because the chemistry of these elements is so much alike. Referring to a graph like that of Fig. 165 it was found that to make the line continuous there should be fourteen rare earth elements; also a homologue of zirconium between barium and tantalum. Thirteen of these positions could be filled from rare earth metals then known. The homologue of zirconium (hafnium) was found by Coster and Hevesy,* and Hopkins† has reported the discovery of the remaining rare earth (61), naming it illinium.

REFERENCES

Isotopes. F. W. Aston.
Introduction to Modern Physics. Richtmyer.
Introduction to Contemporary Physics. Darrow.
Molecular Physics. J. A. Crowther.

PROBLEMS

1. A beam of cathode rays was deflected into an arc having a radius of curvature of 15 cm. by a magnetic field of 4.7 e.m.u. An electric field of 48.8 volts per cm. was required to bring the path of the rays back to its original position (1 volt per cm. = 10^8 e.m.u. per cm.).

(*a*) What is the velocity of the rays?

(*b*) Using $e = 1.59 \times 10^{-20}$ e.m.u., calculate the mass of an electron.

2. Calculate the Avogadro number using Planck's value of e from radiation data, 4.69×10^{-10} electrostatic units.

* Nature, **111**, 79 (1923).

† J. Am. Chem. Soc., **48**, 1585 (1926).

3. The mass spectrum of a mixture of carbon dioxide and methane gave lines which corresponded to the following ratios of mass to number of charges.

6, 8, 12, 13, 14, 15, 16, 28, 32, 44

Suggest positive ions which may be responsible for each of these lines.

4. An investigation of the wave-lengths of the K_α lines in the X-ray spectra of various elements gave for zinc (atomic number 30) $\lambda_{K_\alpha} = 1.445$ Å and for cobalt (atomic number 27) $\lambda_{K_\alpha} = 1.798$ Å. A third element showed a third order reflection from a rock-salt crystal ($d = 8.454 \times 10^{-8}$ cm) at $\theta = 36.7°$. What was the third element?

CHAPTER XXII

RADIOACTIVITY

Discovery of Radioactivity. The first radioactive substance was discovered by Henri Becquerel,* in 1896. It had been shown by Roentgen, in the previous year, that the bombardment of the walls of a vacuum tube by the cathode stream gives rise to a new type of rays, which, because of their puzzling characteristics, he called X-rays. The portion of the tube where these rays originate was observed to fluoresce brilliantly, and it was at once assumed that this fluorescence might be the cause of the new type of radiation.

Many substances were known to fluoresce under the stimulus of the sun's rays, and it was natural, in the light of Roentgen's discovery, that all substances which exhibit fluorescence should be subjected to careful examination. Among those who became interested in these phenomena was Becquerel. He studied the action of a number of fluorescent substances, among which was the double sulphate of potassium and uranium. This salt, after exposure to sunlight, was found to emit a radiation capable of affecting a carefully protected photographic plate. Further investigation proved that the fluorescence had nothing to do with the photographic action, since both uranous and uranic salts were found to exert similar photographic action, notwithstanding the fact that uranous salts are not fluorescent. The photographic activity of both uranous and uranic salts was found to be proportional to their content of uranium. Becquerel also showed that preliminary stimulation by sunlight was wholly unnecessary. Uranium salts which had been kept in the dark for years were found to be just as active as those which had been recently exposed to brilliant sunlight.

The properties of the rays emitted by uranium salts differ in many respects from those of the X-rays. The rate of emission of the radiation from uranium remains unaltered at the highest or the lowest obtainable temperatures. The entire behavior of these salts justifies the conclusion that the continuous emission of penetrating rays is a specific property of the element uranium itself. This property of spontaneously emitting radiations which are capable of penetrating substances opaque to ordinary light is called *radioactivity*.

* Compt. rend., **122**, 420 (1896).

Discovery of Radium. Shortly after the discovery of the radioactivity of uranium, the element thorium and its compounds were also found to be radioactive. As a result of a systematic examination, by Mme. Curie,* of minerals known to contain uranium or thorium, it was learned that many of these were much more radioactive than either uranium or thorium alone. Thus, pitchblende, one of the principal ores of uranium, was found to be four times more active than uranium alone, and chalcolite, a phosphate of copper and uranium, was found to be at least twice as active as uranium. On the other hand, when a specimen of artificial chalcolite, prepared in the laboratory from pure materials, was examined, its activity was found to be proportional to the content of uranium. Mme. Curie concluded from this result that natural chalcolite and pitchblende must contain a minute amount of some substance much more active than uranium.

With the assistance of her husband, Mme. Curie undertook the task of separating this unknown substance from pitchblende. Pitchblende is an extremely complex mineral and its systematic chemical analysis calls for skill and patience of a high order. Without entering into details as to the analytical procedure, it must suffice here to state the results obtained. Associated with the bismuth occurring in pitchblende, a very active substance was discovered, to which Mme. Curie gave the name polonium in honor of her native land, Poland. In like manner, an extremely active substance was found associated with barium in the alkaline earth group. This substance was called radium because of its great radioactivity.

The isolation of pure polonium is extremely difficult, and sufficient quantities have not been obtained to permit determinations of its physical properties, but the isolation of radium in relatively large amounts is readily accomplished. Several tons of high-grade ore are required, however, to produce 1 gram of pure radium. The pure bromides of radium and barium are prepared together, and the two salts are then separated by a series of fractional crystallizations. That the salts of barium and radium are very similar in chemical properties is shown by the fact that they separate together from the same solution. The atomic weight of radium has been determined by several investigators, the accepted value being 226.

In 1910, Mme. Curie succeeded in obtaining metallic radium.† It is a metal possessing a silvery luster, which dissolves in water with energetic evolution of hydrogen and tarnishes rapidly in air with the formation of the nitride.

* Compt. rend., **126**, 1101 (1898).

† Compt. rend., **151**, 523 (1910).

Measurement of Radioactivity. Action on a photographic plate through opaque paper constitutes one of the simplest qualitative tests for the radioactivity of a substance. Days or weeks are needed for preparations of low activity.

Some materials such as zinc sulphide become luminous when exposed to radiation from a radioactive material, and the intensity of this radioluminescence is roughly proportional to the radioactivity. When examined with a lens in a simple instrument called a spinthariscope, the luminescence is seen to consist of a series of scintillations caused by the bombardment of α-particles on the zinc sulphide. Practical use of this phenomenon is made in luminous paints, which are used for luminous dials of watches. A low-grade material of feeble radioactivity is mixed intimately with zinc sulphide and the resulting scintillations are so frequent as to produce a uniform glow to the unaided eye.

The best quantitative measure of radioactivity is obtained from ionization. The radioactive material sends out radiations which ionize the air, and when an electrostatic field of the proper voltage is applied, the resulting current is a measure of the number of ions and the number of ions, in turn, furnishes a measure of the radioactivity. Two parallel plates are charged to a few hundred volts, one being connected to the ground and the other being connected through an electrometer or electroscope to the ground. It is necessary to apply sufficient voltage to reach the *saturation current*, indicated by the horizontal line in Fig. 166. Below this voltage the ions tend to recombine before reaching the electrodes, and the current is small. As the difference of potential is increased, the ions move faster, more of them reach the electrodes before recombining, and the current increases. Over certain regions, Ohm's law applies, the current being directly proportional to the voltage. When the saturation current is reached, all the ions are drawn to the electrode without recombining and a further increase in voltage cannot increase the current. At much higher voltages, however, the ions can produce other ions by collision and lead to a much greater current as indicated by the steep curve at the end. Only in the region of saturation current is the current a true measure of the number of ions produced by the radioactivity. The method is so sensitive that it is possible to detect 1×10^{-11} gram of radium, and it is more sensitive, in fact, than methods depending on the balance or on the spectroscope.

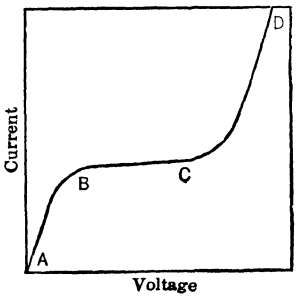


FIG. 166

Nature of the Radiations. The radiations emitted by radioactive substances are of three different types, as determined by their penetrating power and their deflection in electrostatic and electromagnetic fields.

Rutherford named these three distinct types of radiation the α-, β-, and γ-rays, respectively. The penetrating powers of the α-, β-, and γ-rays may be approximately expressed by the proportion 1 : 100 : 10,000; that is, the β-rays are 100 times more penetrating than the α-rays, and the γ-rays are 100 times more penetrating than the β-rays.

The general characteristics of the three kinds of rays may be briefly summarized as follows: —

(1) *α-Rays.* The α-rays consist of particles with a mass of four, having two positive charges and moving with speeds approximately one-tenth as great as that of light. The velocity, charge and mass were determined with the same type of apparatus described on p. 559. These particles have been shown to be identical with helium atoms carrying two positive charges of electricity. They are appreciably deflected from a rectilinear path by magnetic and electric fields. They possess great ionizing power, but relatively little penetrating power, or photographic action. The depth to which an α-particle penetrates a homogeneous absorbing medium before losing its ionizing power is known as its "range." The range has been found to be proportional to the cube of the initial speed of the α-particle, and is one of the properties characteristic of each of the radioelements emitting α-rays.

(2) *β-Rays.* The β-rays consist of negatively charged particles moving with speeds varying from two-fifths to nine-tenths of the speed of light. They are the same as cathode rays except that the electrons are moving much faster. Whereas the α-particles emitted by a particular radioelement have a definite velocity, the corresponding β-ray emission consists of a flight of particles having widely different speeds. The penetrating power of the β-rays is conditioned by the speed of the particles, those which move most rapidly possessing the greatest penetrating power. The ionizing action of the β-rays is much weaker than that of the α-rays.

(3) *γ-Rays.* The γ-rays are identical with X-rays, except that they have shorter wave-lengths varying from about 1×10^{-8} centimeter for the rays of low penetrating power, to about 1×10^{-9} centimeter for the most penetrating rays. Obviously, γ-rays cannot be deflected from a rectilinear path by either electric or magnetic fields.

The Radium Emanation (Radon). When a specimen of radium bromide is gently heated, or when a current of air is bubbled through a solution of a radium salt, a small volume of an exceedingly radio-

active gas is obtained. Rutherford, to whom we are indebted for much of our knowledge of this interesting substance, named it, somewhat vaguely, the "emanation." In 1911, Ramsay and Gray,* making use of a special quartz micro-balance, sensitive to one-millionth of a milligram, succeeded in determining the mass of a known volume of pure emanation. On the assumption that the gas is monatomic, they computed the average value of its atomic weight to be 222. The value of the atomic weight of the emanation, taken together with its chemical inertness, served to determine its position in the group of non-valent elements in the periodic table. In order to emphasize its relationship to the inert gases the International Committee on Chemical Elements proposed that it be named "radon."

The following crucial experiment, carried out by Rutherford and Royds,† with radon, furnished conclusive evidence that the α-particle consists of an atom of helium carrying two positive charges. A glass bulb was blown with walls thin enough to permit the passage of the α-particles, but of sufficient strength to withstand atmospheric pressure. The bulb was filled with radon under pressure, and then enclosed in an outer glass tube, to which a spectrum tube had been sealed. On exhausting the outer tube, and examining the spectrum of the residual gas, no evidence of helium was obtained until after an interval of twenty-four hours. After four days, the yellow and green lines characteristic of helium were plainly visible, and at the end of the sixth day the complete spectrum of the element was obtained. The unavoidable conclusion from this experiment is that the presence of helium in the outer tube must have been due to the α-particles which were projected through the thin walls of the inner tube. In another experiment, the inner tube was filled with pure helium under pressure, while the exhausted outer tube was examined for helium. No trace of the gas could be detected spectroscopically, even after an interval of several days, thus proving that the helium detected in the first experiment must have resulted from the α-particles which had been shot out from the radon with sufficient energy to penetrate the thin walls of the inner tube. These experiments leave no room for doubt that an α-particle becomes a helium atom when its positive charge is neutralized.

There is an abundance of experimental evidence which proves that only one α-particle is expelled from each atom of radium in the formation of radon. The process may be represented by the equation,

$$\mathrm{Ra} = \mathrm{Rn} + \mathrm{He}.$$

* Proc. Roy. Soc., **A 84**, 536 (1911).

† Phil. Mag. (**6**), **17**, 281 (1909).

Since the atomic weight of radium is 226, and that of helium is 4, it follows that the atomic weight of radon should be 222. This, it will be remembered, is exactly the value which Ramsay and Gray obtained for the atomic weight of radon.

Taken mass for mass, radon is much more radioactive than the radium from which it was derived, but the activity is found to diminish rapidly with time, and practically to have disappeared at the end of a month.

A radium salt loses the greater part of its activity when the emanation is removed, but the radium recovers its activity at precisely the same rate as the radon loses its activity. In other words, when the processes of decay and recovery are examined quantitatively, it is found that they are complementary, and that the total radioactivity remains unaltered. The decay of radon and recovery of radium both follow an exponential law which is expressed by the following equations:

$$I_t = I_0 e^{-\lambda t}, \qquad \text{(decay)} \qquad (1)$$

and

$$I_t' = I_0'(1 - e^{-\lambda t}), \quad \text{(recovery)} \qquad (2)$$

where I_0 is the initial activity, I_t the activity after a time t, λ a constant, known as the *radioactive constant*, and e the base of the natural

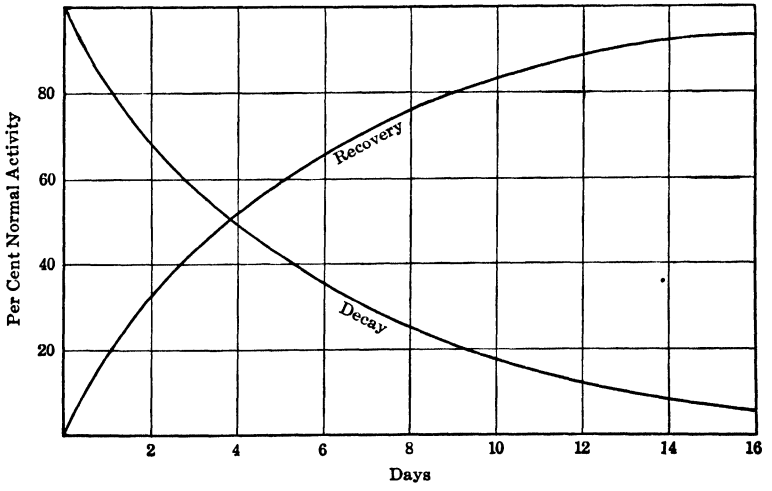


FIG. 167

system of logarithms. The decay curve of radon, and the recovery curve of the activity of radium, as measured by the α-rays, are shown in Fig. 167. From these curves, it is apparent that while the radon is

decaying from day to day, the radium is in turn producing a fresh supply.

Radioactive Disintegration. The disintegration of the radioelements involves changes in the character of the atoms whereas ordinary chemical reactions involve changes only in the arrangement of atoms in molecules. The energy changes accompanying atomic disintegration are much greater than those accompanying chemical reactions and the disintegrations are not affected by temperature, the rate of disintegration being the same at liquid air temperatures and at 1000° C.

It is supposed that, on the average, a definite proportion of the atoms of each radioelement becomes unstable at a given time, and as a result of this instability, an α-particle or a β-particle is expelled with great violence. The γ-rays are probably secondary effects produced by β-rays in a manner similar to the production of X-rays by cathode rays. Since the number of atoms disintegrating is proportional to the number of atoms present, the simple equations for the unimolecular reaction apply with exactness. In the equation

$$n_t = n_0 e^{-\lambda t}, \tag{3}$$

n_t refers to the number of atoms at time t, and n_0 to the number at the beginning of the experiment when $t = 0$, and λ refers to the radioactivity constant, or fraction of atoms undergoing disintegration in a unit of time, provided the unit of time is so small that the total number is essentially unchanged. The intensity, I, of radioactivity, as measured for example by the ionization current, may be substituted for n in the formula, giving equation (1).

The *period of half life*, $t_{\frac{1}{2}}$, is frequently used instead of the radioactivity constant λ. As explained on p. 323,

$$t_{\frac{1}{2}} = \frac{0.6932}{\lambda}. \tag{4}$$

The *average life* represents "the sum of the separate periods of future existence of all the individual atoms, divided by the number in existence at the starting time." Integration shows that the period of average life, t_{average}, is simply the reciprocal of the radioactivity constant, λ. Thus

$$t_{\text{average}} = \frac{1}{n_0}\int_0^\infty n_t\, dt = \frac{1}{\lambda} \tag{5}$$

where λ is defined by the equation

$$-\frac{dn}{dt} = \lambda n. \tag{6}$$

Radioactive Equilibrium. It was shown that radon is being produced continuously by disintegration of radium and that the radon, in turn, is continuously decomposing into radium A. The rate at which radon is produced from a quantity of radium is given by the expression $\lambda_1 n_1$, where n_1 is the number of radium atoms, and λ_1 is the disintegration constant of radium; the rate at which it decomposes is given by the expression $\lambda_2 n_2$ where n_2 is the number of radon atoms and λ_2 is the disintegration constant of radon. When the rate of production of a radioelement from its parent element is equal to its rate of disintegration into the next succeeding element of the series, the substance is said to be in radioactive equilibrium. Under equilibrium conditions, radon is decomposing at the same rate that it is being formed and

$$\lambda_1 n_1 = \lambda_2 n_2 \tag{7}$$

or

$$\frac{n_1}{n_2} = \frac{\lambda_2}{\lambda_1} = \frac{\text{average life}_1}{\text{average life}_2} = \frac{\text{half-life}_1}{\text{half-life}_2}. \tag{8}$$

These formulas hold for any radioelements in a state of equilibrium, and each product accumulates until a fixed ratio with respect to the parent element is attained, this ratio being the same as the ratio of average lives, or inversely as the ratio of the two disintegration constants. This law holds rigidly only when the average life of the original material is long, compared to the lives of the disintegration products in the series.

Radioactive equilibria may be compared to equilibria existing in a series of reservoirs, each reservoir being supplied with an inlet pipe, and an outlet pipe leading to the next lower reservoir. When the inlet is large and the outlet small the level in the reservoir is high, for only under these conditions can the hydrostatic pressure offset the handicap of the smaller outlet and cause the reservoir to empty at the same rate at which it fills. When the outlet pipe is large, the level in the reservoir is low. Likewise when the disintegration constant has a large value, the radioelement is present only in small quantities.

Successive reactions similar to these are found in ordinary chemical reactions, and when an intermediate product is formed as fast as it decomposes a *steady state* is said to exist. The mathematical treatment of the differential equations becomes more difficult when the first member of the disintegrating series has a comparatively short period of life and the rate of supply of material cannot be considered constant.

Counting the α-Particles. Rutherford and Geiger* devised an electrical method for counting the α-particles. In their experiment the

* Proc. Roy. Soc., **A 81**, 141 (1908).

source of the α-particles was a small disc which had been exposed to the radium emanation for some hours. This disc was placed in an evacuated tube, at a measured distance from a small aperture of known cross section. The aperture was closed with a thin plate of mica through which the α-particles could pass with ease. After passing through the mica plate, the α-particles entered an ionization chamber filled with air at reduced pressure, and fitted with two charged metal plates connected with appropriate apparatus for measuring ionization currents. Whenever an α-particle entered the ionization chamber, a momentary current passed, producing a sudden deflection of the needle of the electrometer. By counting the number of throws of the needle occurring in a definite interval of time, the total number of α-particles passing through the ionization chamber could be determined. Knowing the distance of the source of the radiations from the aperture, together with the area of the aperture, the total number of α-particles emitted by the radioactive disc in a given time could be computed. Rutherford and Geiger thus found that 1 gram of radium emits very nearly 3.4×10^{10} α-particles per second. Having determined the total number of α-particles emitted, it remained only to measure the total charge in order to calculate the charge carried by a single α-particle. From a series of very consistent measurements, the charge carried by a single α-particle was found to be 9.3×10^{-10} electrostatic unit. Since the fundamental charge e has been shown to be 4.774×10^{-10} electrostatic unit, it follows that the α-particle carries two charges of electricity. Deflections in an electrostatic field show that the charges are positive.

Avogadro's Constant from Radioactivity Data. Since it has been proved that each α-particle is transformed into a helium atom, and since we can count the α-particles and measure the volume of helium, we have at once a direct method for determining the number of molecules in a gram-molecule of helium, and this number is the Avogadro constant.

Rutherford and Boltwood* found that 1 gram of radium produces 0.107 cubic millimeter of helium per day, measured under standard conditions, and combining this fact with the fact that 1 gram of radium emits 3.4×10^{10} α-particles per second, a simple calculation gives 6.16×10^{23} for the Avogadro number, a value which is in good agreement with other determinations of this constant obtained from entirely independent measurements.

The Origin of Radium and the Uranium Disintegration Series. As the result of a large amount of careful experimental work, it has been shown that radium is but one of a series of radioelements, each of which

* Phil. Mag., **22**, 586 (1911).

is formed by the atomic disintegration of the preceding member of the series, in precisely the same manner as radon is formed from radium.

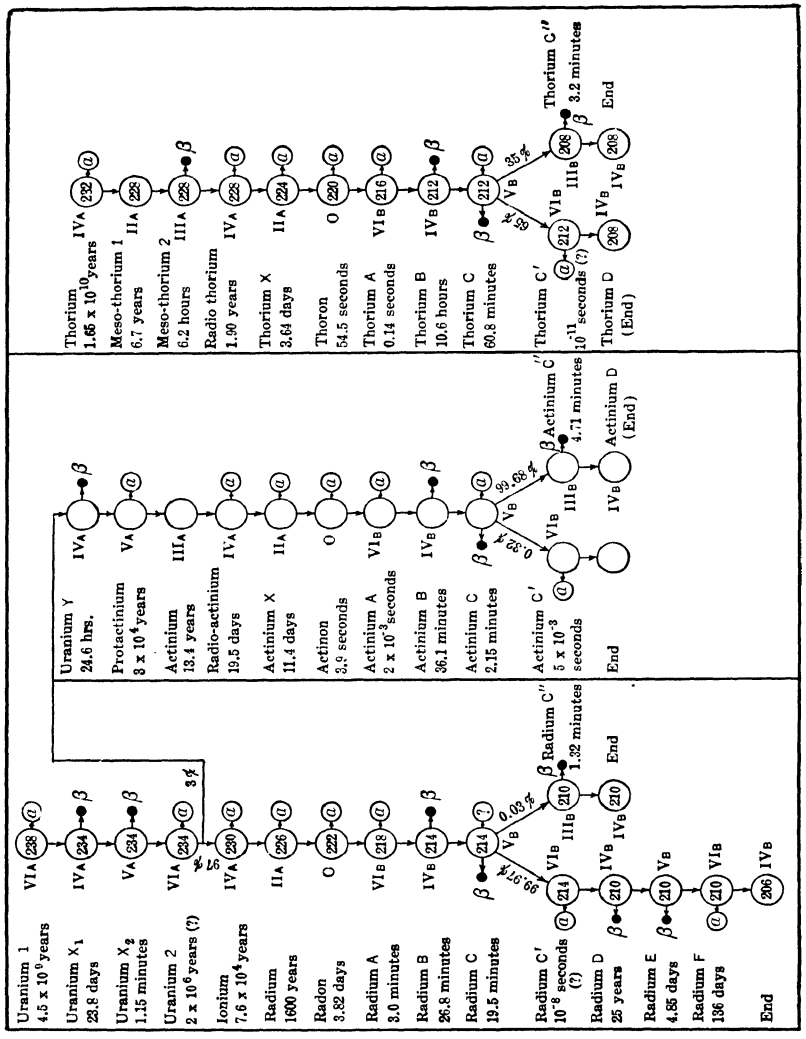
Radium is not the direct product of uranium, but rather is the fifth successive member of the disintegration series which has its origin in uranium. Uranium changes into UX_1, with the simultaneous expulsion of an α-particle and a consequent loss of four units in atomic weight. The element uranium disintegrates at an exceedingly slow rate, the probable value of its average life being 6,500,000,000 years. The element UX_1 changes with the emission of a β-particle, and hence without loss of weight, into the element UX_2, which, because of its brief average life of 1.65 minutes, is sometimes called brevium. Two other radioelements, U2 and Ionium, with periods of average life of 2,900,000 and 109,000 years, respectively, are formed in succession from UX_2 before the element radium is formed from ionium.

If a negatively charged wire is introduced into a vessel containing radon, an extremely radioactive substance, known as the "active deposit," is condensed upon its surface. This deposit, which can be detected by neither balance nor microscope, has been found to consist of the successive disintegration products of radon. The atomic disintegration of radon takes place in eight distinct successive stages, the first four radioelements of the active deposit being characterized by very short average lives, ranging from 38.5 minutes for RaB, to 1.4×10^{-8} second for RaC', while the remaining elements of the series undergo transformation at a much slower rate, their average lives varying from 7.00 days to 36 years. It is of interest to note that RaF has been found to be identical with polonium, the first radioelement to be isolated from pitchblende by Mme. Curie.

Although lack of space precludes a detailed consideration of thorium and actinium, it should be mentioned that each of these elements disintegrates in a manner similar to that of uranium, giving rise to a series of interesting radioelements which, in general, are shorter lived than the members of the uranium series. Taking the three series together, the science of radioactivity now embraces nearly forty elements each of which is endowed with specific properties and with periods of existence varying from thousands of millions of years, on the one hand, to a small fraction of a second, on the other. Soddy says of the radioelements, "It is unlikely that any more of these unstable elements remain to be discovered, unless some entirely unknown and unsuspected source of radioactive materials is found." The accompanying table gives the three disintegration series.

The numbers within the circles denote the atomic weights of the elements; the small circles and dots at the right of the larger circles

DISINTEGRATION SERIES OF THE RADIOELEMENTS



indicate the character of the radiation given out at each stage of the disintegration process. The half life, $0.693/\lambda$, of each element in the series is given below the name of the element. The roman numerals refer to the groups in the periodic table.

The Radioelements and the Periodic Table. The problem of placing the newly discovered radioelements in the periodic table remained unsolved until 1913, when Fajans* and Soddy,† working independently, discovered an important generalization concerning the changes in chemical properties resulting from the expulsion of α- and β-particles during radioactive transformations. This displacement law may be stated as follows: — *The expulsion of an α-particle causes a radioactive element to shift its position in the periodic table two places in the direction of decreasing atomic weight, whereas the emission of a β-particle causes a shift of one place in the opposite direction.* This generalization not only agrees with our present theory of atomic structure, but may be shown to be a necessary consequence of this theory.

The loss of an α-particle, or helium atom, involves a loss of 4 units in atomic weight and of 2 units of positive electricity from the nucleus of the atom. In consequence of this loss, the atomic number is diminished by 2 units, and the resulting new element finds a place in the periodic table two groups to the left of that occupied by the parent element. On the contrary, while the expulsion of a β-particle, or electron, involves practically no change in mass, the nucleus of the parent atom suffers a loss of 1 unit of negative electricity. This loss is equivalent to a gain of 1 unit of positive electricity, or to an increase of 1 unit in the atomic number, and in consequence, the position of the new element in the periodic table is shifted one group to the right of that occupied by the parent element, with a corresponding change in valence.

Soddy's arrangement of all the radioelements in accordance with this generalization is shown in Fig. 168. Thus, starting with the element uranium in Group VIA, we may follow the successive steps in the radium disintegration series which were discussed in the preceding paragraph. The element UX_1, resulting from U by the loss of an α-particle, is placed in Group IVA. This element in turn undergoes a β-ray change, producing the element UX_2, which is accordingly placed in Group VA. The element UII in Group VIA is formed from UX_2 by β-ray disintegration, and the element Io results from the loss of an α-particle by UII_0 with a consequent shift to the left into Group IVA. A similar loss of an α-particle by Io brings us to the element Ra,

* Physik. Z., **14**, 49 (1913).

† Chem. News, **107**, 97 (1913).

in Group IIA. In the successive steps of this disintegration from U to Ra, 3 α-particles, or 12 units of atomic mass, are lost, and the atomic weight of Ra, as calculated from that of U, agrees with the atomic weight found by direct experiment. In like manner, the re-

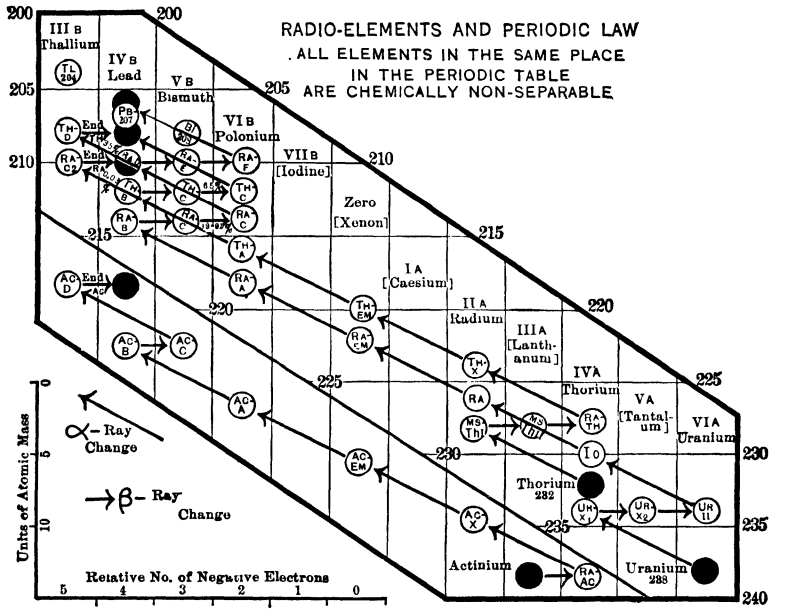


FIG. 168

maining stages of the disintegration may be followed to the end-product in Group IVB.

Perhaps the most striking feature in the table is the occurrence of several different elements in the same place, as for example in Group IVB, where in the place occupied by the element Pb, we also find RaB, RaD, ThB, and AcB, together with four other elements to which no names have been assigned, but which are none the less stable end-products. The individual members of such a group of elements occupying the same place in the periodic table are therefore *isotopic*. Among the radioelements then it is possible to observe isotopes in the making.

Just as it is possible to have elements with identical chemical properties but differing in atomic weight, so it is also possible to have elements possessing different chemical properties with the same atomic weight. Such elements have been called *isobars*. The product of a radioactive change in which a β-particle is lost is an isobar of the

parent element, since its position in the periodic table has been shifted without undergoing appreciable change in mass, while its chemical properties have changed to correspond with its new position in the table.

Applications of Radioactivity. Experiments on radioactivity have led to important advances in several different fields. Rutherford measured the angle through which α-particles are deflected when they strike against thin sheets of metal and discovered that some of the particles are scattered through surprisingly large angles. The particles have a mass four times that of the hydrogen atom and are moving with one-tenth the velocity of light, and yet a few of them are reflected backward through angles between 90° and 180°. Such violent changes in momentum can be explained only on the assumption that the targets of these occasional α-particles are vastly more dense than any ordinary material. These facts led Rutherford to the nuclear theory of the atom, which constitutes the foundation of our modern conception of atomic structure. He concluded that atoms have practically all their mass concentrated in a nucleus which is about one-hundred-thousandth the size of the atom itself and that these abnormal reflections of α-particles are caused by direct hits against the atomic nucleus. The nuclear theory will be discussed in the next chapter.

The paths of individual α-particles or β-particles are rendered plainly visible by shooting the particles into a chamber containing supersaturated water vapor. Each α-particle produces about 100,000 gas ions and each of these ions condenses a droplet of water. This "cloud-track" method was devised by C. T. R. Wilson. The α-particles travel in straight lines, except that occasionally a branched track is found which indicates a direct hit on the nucleus of an atom.

The study of reaction mechanisms as well as of atomic structure has been aided by experiments with the radioelements. Lind determined the ratio of the number of molecules M reacting to the number of pairs of ions N produced, and found a stoichiometric relation in many reactions. The number of molecules reacting is ascertained by pressure changes, or by chemical analysis, and the number of ions is calculated from ionization data. To illustrate the interpretation of such data, the action of α-particles on a mixture of hydrogen and oxygen may be cited, where it is found that four molecules of water are produced for each pair of ions.* Equations involving the attachment of hydrogen or oxygen molecules to oxygen or hydrogen ions, giving $(H_2O_2H_2)^+$ and $(H_2O_2H_2)^-$, and the further neutralization and decomposition to give water, can be written so as to produce four

* Lind, "Chemical Effects of Alpha Particles and Electrons, Second edition, p. 100.

molecules of water from each pair of ions. Accordingly these equations are thought to give a plausible mechanism for the reaction.

Chemical reaction may follow after gas ionization, whether the ionization is produced by α-rays or by electrical discharge, and the whole study of the electrochemistry of gases* has been greatly aided by the information obtained from radioactivity experiments which can be carried out under more easily controlled conditions. The formation of ozone, the synthesis and decomposition of hydrocarbons, the oxidation of nitrogen, and many other reactions can be effected by the passage of electricity through gases.

The use of radio-indicators offers a new solution for certain analytical problems.† The test for radioactivity is so much more sensitive than other physical or chemical tests that the minutest amount of material can be detected. The solubility of a difficultly soluble lead salt may be determined by placing a trace of radio-lead in a saturated solution and allowing the radio-lead to distribute itself between the solution and the solid in proportion to the solubility of the lead. The distribution ratio can be easily and accurately determined by measuring the intensity of radioactivity. Again, it is possible with radio-indicators to determine the actual number of atoms of lead or other element exposed in a crystal and accordingly the absolute surface can be calculated.

The medical uses of radioactivity are well known. Although serious burns can be produced by radium, it is possible under properly controlled conditions to destroy early cancerous tissue and other abnormal growths. For such purposes radon is used. It is collected by bubbling air through a solution of a radium salt and condensing out the radioactive gas at low temperatures in very small glass tubes which are then sealed off.

REFERENCES

Treatise on Physical Chemistry, Chapter XXI. Taylor.
The Interpretation of Radium. Soddy.
Radiations from Radioactive Substances. Rutherford, Chadwick, and Ellis.
Radio-Elements as Indicators. Paneth.
The Chemical Effects of Alpha Particles and Electrons. Lind.
Radioactivity. Fajans.

* Lind, Trans. Am. Electrochem. Soc., **53**, 25 (1928); J. Am. Chem. Soc. **51**, 2819 (1929); Brewer and co-workers, J. Phys. Chem., **34**, 2343 (1930), and earlier papers.

† Paneth, " Radio-Elements as Indicators "; Daniels, Mathews, and Williams, " Experimental Physical Chemistry," p. 268.

PROBLEMS

1. The disintegration constant of radon is 2.097×10^{-6} sec.$^{-1}$.

(*a*) What fraction of the original material will be left after 3.825 days? (*b*) What is the average life? (*c*) What is the period of half-life? *Ans.* (*b*) 5.518 days.

2. A certain radioelement has a radioactivity constant of 1.654×10^{-6} sec.$^{-1}$.

(*a*) What is its period of half-life?

(*b*) What is its average life?

(*c*) How long will it take for 99 per cent of the element to disintegrate?

(*d*) What is the name of this radioelement?

3. A sample of radon lost $\frac{1}{3}$ of its activity in 2 days and 6 hours. At what time will it have lost $\frac{2}{3}$ of its activity? *Ans.* 6 days, 2.3 hours.

4. A hospital maintained a solution containing 0.250 g. of radium as a source of radon for therapeutic purposes. The radon was pumped off under reduced pressure once a week. $\lambda_{radon} = 2.097 \times 10^{-6}$ per sec.

(*a*) How many grams of radon was obtained each week?

(*b*) What volume would it occupy under standard conditions of temperature and pressure?

5. The *curie* is defined as the quantity of radon in equilibrium with one gram of radium. From the periods of half-life given in the table on p. 582, calculate:

(*a*) The weight in grams of 1 curie.

(*b*) The volume occupied by 1 curie under standard conditions of temperature and pressure. *Ans.* (*a*) 6.425×10^{-6} g. (*b*) 0.6483 cu. mm.

6. Calculate the weight of radium *E* in equilibrium with 1 g. of radium *D* from the values of half-life given in the table on p. 582.

7. Give the details of the calculation of the Avogadro constant, based on the facts that 1 g. of radium produces 0.107 cu. mm. of helium per day (measured at 0° and 760 mm.) and emits 3.4×10^{10} α-particles per sec.

8. Thorium *B* is an isotope of lead, and thus has nearly identical chemical and physical properties. A given quantity of thorium *B* was mixed with a lead salt containing 10 milligrams of lead, taken into solution and precipitated as the chromate. Ten cc. of the supernatant liquid, when evaporated, gave a residue which was $\frac{1}{24000}$ as active as the original quantity of thorium *B*. What is the solubility of lead chromate in mols per liter? *Ans.* 2×10^{-7} mols per liter.

9. The weight of lead in a sample of uraninite from the Black Hills of South Dakota was found to be 22.8 per cent of the weight of the uranium.

(*a*) Assuming that all of the lead had its origin in the disintegration of uranium, what fraction of the original uranium atoms still remained?

(*b*) Taking the radioactivity constant of uranium as 4.66×10^{-18} per sec. calculate the age of this mineral, and thus obtain a minimum value for the age of the earth. *Ans.* 1,600,000,000 years.

10. Suggest a mechanism by which four molecules of water might be produced per ion pair, in a mixture of hydrogen and oxygen.

11. Actinium emanation comes in the group of rare gases, having zero valence. It loses an α-particle, the product loses another α-particle and then the new radioelement loses a β-particle. (*a*) To what group in the periodic table does this radioelement belong? (*b*) Describe briefly its physical and chemical problems.

CHAPTER XXIII

ATOMIC STRUCTURE

Nuclear Theory of the Atom. We have described four fundamental experiments on which theories of atomic structure are based. The disintegration of radioelements indicates that the nuclei of heavy atoms contain helium atoms and electrons. The occasional, abnormal deflection of α-particles shows that the mass of the atom must be concentrated in a nucleus occupying but a small fraction of the total atom. The mass spectrograph gives a measure of the mass of the nucleus, and the X-ray measurements of the atomic number reveal the number of excess positive charges on the nucleus.

Negative electricity occurs only as electrons, but positive electricity probably occurs in two units, the smaller of which is the hydrogen nucleus or *proton*, and the larger of which is the helium nucleus. The nuclei of all the other atoms are thought to be built up from these units, and the old hypothesis of Prout proposed in 1815, according to which all elements are composed of hydrogen, is thus revived and accepted. Many elements have atomic weights which are far from being whole numbers because they are mixtures of isotopes.

The following examples will suffice to show how the nuclei of atoms are built up from the fundamental units. The atomic mass is determined by the total number of protons in the atom and there is good evidence that these are grouped as far as possible into secondary units, the helium nuclei, which contain four protons and two electrons. The atomic number is then the difference between the total number of protons and the total number of electrons in the nucleus.

Transmutation. We have seen that the heaviest elements undergo radioactive disintegration spontaneously and it is possible to disintegrate the light elements artificially. Rutherford and Chadwick* succeeded in knocking protons out of the nuclei of nitrogen atoms. The experimental evidence for this phenomenon is rather indirect, but it seems to be fully established. The α-particles have a definite range in nitrogen of about 7 centimeters, but some flashes of light, apparently due to the impact of fast-moving particles, can be detected on a sensitive screen at much greater distances. Deflections in a magnetic field

* Phil. Mag. (6), **44**, 417 (1922); Rutherford, J. Chem. Soc., **121**, 400 (1922).

STRUCTURE OF ATOMIC NUCLEI

Element	Total Number of Protons in Nucleus	Total Number of Electrons in Nucleus	Atomic Number
Hydrogen	1	0	1
Helium	4	2	2
Lithium^{6}	6	3	3
Lithium^{7}	7	4	3
Lithium	Mixture of Li^{7} and Li^{6} having average atomic weight of 6.94		
Beryllium	9	5	4
Boron^{10}	10	5	5
Boron^{11}	11	6	5
Boron	Mixture of B^{10} and B^{11} having average atomic weight of 10.82		
Fluorine	19	10	9
Neon^{20}	20	10	10
Neon^{22}	22	12	10
Neon	Mixture of neon^{20} and neon^{22} having average atomic weight of 20.2		
Chlorine^{35}	35	18	17
Chlorine^{37}	37	20	17
Chlorine	Mixture of Cl^{35} and Cl^{37} having average atomic weight of 35.456		

indicate that the particles which cause these scintillations are protons. It might be expected that, if an α-particle hits a hydrogen atom squarely, the latter with a mass one-fourth as great could travel four times as far, or 28 centimeters. As a matter of fact, in pure nitrogen, flashes can be detected up to a distance of 40 centimeters. Such a great range is explained on the hypothesis that the nucleus of the nitrogen atom is actually altered by the collision with the α-particle and intra-atomic energy is released which drives the proton out with great additional force.

The light elements have been disintegrated by means of α-particles in this way, except those with weights which are integral multiples of four. The fact that carbon (12), oxygen (16), and other elements whose atomic weights are multiples of four are not disintegrated, supports the view that these nuclei contain only helium nuclei, and that atomic nuclei are composed chiefly of helium nuclei. Only in case a nucleus contains one, two or three extra protons can the atom be disintegrated by means now available. The elements higher than phosphorus in atomic number have not yet been disintegrated.

These experiments on the disintegration of light atoms form the only well-tested basis for the hope of harnessing intra-atomic energy. It is noteworthy that the source of the extra atomic energy here is probably the combination of the α-particle with the nitrogen nucleus,

and this gain is diminished by the amount of energy necessary to expel the proton. Possibly the whole process may be represented by the equation

$$He^4 + N^{14} = O^{17} + H^1 + \text{Energy}.$$

It can be calculated that an electron falling through a potential difference of six million volts is about equivalent in kinetic energy to a swiftly moving α-particle, and so could perhaps be used to initiate such changes as that just referred to, but this voltage is beyond the limit of present experimental realization. Also, the proportion of direct hits is so very small that an enormous number of projectiles must be used to get one successful explosion. It seems unlikely that artificial disintegration can ever be of practical importance.

There is some evidence that, under certain conditions, in stars the light elements are condensing into heavier elements. The hottest stars contain only hydrogen and helium and the spectrograph reveals the heavier elements only in the cooler stars. Moreover Millikan and Cameron* conclude from measurements of cosmic radiation that these rays are produced by the condensation of helium and hydrogen to give the heavier elements.

With regard to the structure and origin of the elements, one empirical relationship is very clear. The elements of even atomic number are more stable than those of odd atomic number. Harkins† has pointed out that the elements of even atomic number are more stable and hence more abundant in the earth's crust, and that, among the radioactive elements, the even numbered are, in general, longer lived. Thinking that the earth's crust might not give a fair sample, he examined the composition of meterorites and again found a striking preponderance of the elements of even atomic number. It will be emphasized in several connections that the pairing of electrons to give even numbers is very common.

The Packing Effect. It has been stated that the helium nucleus is probably composed of four protons and two electrons. There appears to be a violation of the law of the conservation of mass because a gram-atom of helium weighs 0.029 gram less than four gram-atoms of hydrogen. The electrons are of negligible weight. According to the theory of relativity, however, mass and energy are interconvertible and are related by the equation

$$1 \text{ gram} = 9 \times 10^{20} \text{ ergs}.$$

* Phys. Rev., **33**, 533 (1928).

† J. Am. Chem. Soc. **39**, 856 (1917).

The factor 9×10^{20} is the square of the velocity of light, all quantities being expressed in the c.g.s. system of units. The reaction may be represented by the equation

$$4\ \mathrm{H}(4 \times 1.00778\ \mathrm{g.}) = 1\ \mathrm{He}(4.00216\ \mathrm{g}).$$
$$\Delta H = -0.029 \times 9 \times 10^{20}\ \mathrm{ergs} = 63 \times 10^{11}\ \mathrm{calories}.$$

This energy is much greater than any energy ordinarily available and, according to Millikan, it is evolved in the form of very penetrating cosmic radiation. Not only helium but all the other heavier elements are probably formed from hydrogen in this way, and in every case there seems to be a loss of mass in the formation. The proportional amount of this loss (packing effect)* is greatest for elements with atomic weight about 70 to 80, and less for both heavier and lighter elements.

Extra-Nuclear Structure. The discussions thus far have been concerned with the nucleus. We shall now consider the arrangement of electrons outside the nucleus. As emphasized before, the number of electrons surrounding the nucleus in the neutral atom is exactly equal to the charge on the nucleus, i.e., the atomic number. These electrons are arranged in definite, stable shells or groups, and the number remaining, after inner groups have been at least provisionally completed, determines the valence, the position in the periodic table, and the chemical properties.

Hydrogen has one extra-nuclear electron and helium has two. The first group can include only two electrons, and so lithium with three electrons has to start a new shell with its extra electron. Beryllium with an atomic number of 4 has four electrons, two of which are used in filling the first shell and two of which go into the second shell. Boron has three in the second shell and carbon four, etc. The second shell may have 8 electrons. The third reaches provisional completion with eight, but in heavier elements expands to include eighteen. The properties of the elements in the third and fourth period are the expression of these relationships.

Eight points are naturally represented by a cube with its eight corners, and the static or cubic atom was proposed in 1916 by G. N. Lewis† and elaborated by Langmuir.‡ This model has brought out certain regularities, emphasized chemical properties and led to new views of valence. It is not to be taken literally, however. The

* The quantity called by Aston the *packing fraction* is so expressed as to be most negative in case of the greatest proportional packing.

† J. Am. Chem. Soc., **38**, 762 (1916).

‡ J. Am. Chem. Soc., **41**, 868 (1919).

corner of the cube may be considered as representing the average position of an electron but a much more complicated model is needed to represent the facts of spectroscopy as outlined in the following chapter. In Fig. 169 the cubical atom is illustrated for the first short period from lithium through fluorine. Neon with an atomic number 10 has the two positions in the first shell and all eight positions in the second shell occupied. Its outermost shell is complete, and the next element, sodium, with an atomic number 11, has to start a third shell with one

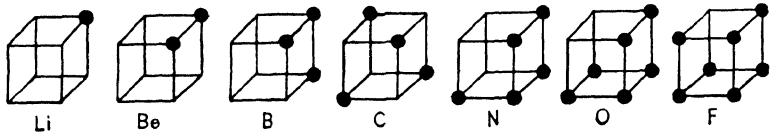


FIG. 169

electron. Magnesium with an atomic number 12 has two electrons in the first shell, eight electrons in the second and two in the third shell. Chlorine has two in the first, eight in the second, and seven in the third. In argon, with an atomic number 18, the third shell is provisionally completed. Potassium with an atomic number 19 starts the fourth shell with one electron, having the inner shells filled successively with two, eight and eight electrons. Calcium has two electrons in the outer shell. With scandium, the number of fourth shell electrons remains two, while the third valence electron begins the expansion of the third group from eight to eighteen.

The number of loose electrons determines the valence and many chemical properties. Helium, neon and argon are all alike in having a completed group of two or eight in their outermost shells, and they are all chemically inert. The similar alkali metals, lithium, sodium and potassium, are alike in having one electron in the outermost shell. Beryllium, magnesium and calcium have two electrons in the outermost shell, while fluorine and chlorine have seven electrons in the outermost shell. The grouping of like elements in the periodic table is thus traced to the similarity in electron arrangement.

The first, second, third and fourth shells are technically known as the K, L, M, N shells. They correspond to the K, L, M, N series in the X-ray spectra discussed on p. 569. K radiation is involved when the target is bombarded with cathode rays of sufficient velocity to displace electrons from the innermost shell. The L series of X-ray spectral lines is emitted when electrons fall back from outer shells into positions in the second shell from which electrons have been displaced by X-ray bombardment, or left vacant when the L electron falls back to the K shell to give a line in the K series.

PERIODIC TABLE

Shell	I	II	III	IV	V	VI	VII	VIII or 0		
1 or K	**1** H 1 0078	... ...	... ...	. ..	. ...	. ..	.. ..	.. ..	. ...	**2** He 4 00
2 or L	**3** Li 6.94	**4** Be 9 0	**5** B 10.8	**6** C 12.00	**7** N 14 01	**8** O 16 00	**9** F 19 0	... ...	... ...	**10** Ne 20 2
3 or M	**11** Na 23 00	**12** Mg 24 32	**13** Al 27.0	**14** Si 28.1	**15** P 31 02	**16** S 32 06	**17** Cl 35 46	. . ..	..	**18** A 39 9
4 or N	**19** K 39.10	**20** Ca 40 08	**21** Sc 45 1	**22** Ti 47 9	**23** V 51 0	**24** Cr 52 0	**25** Mn 54 93	**26** Fe 55.84	**27** Co 58 94	**28** Ni 58.68
	29 Cu 63 57	**30** Zn 65 38	**31** Ga 69.7	**32** Ge 72 6	**33** As 74 93	**34** Se 79 2	**35** Br 79 92	.. ...	.. ...	**36** Kr 82 9
5 or O	**37** Rb 85 44	**38** Sr 87 63	**39** Y 88 9	**40** Zr 91 2	**41** Cb 93 3	**42** Mo 96 0	**43** ..	**44** Ru 101 7	**45** Rh 102.9	**46** Pd 106 7
	47 Ag 107 88	**48** Cd 112 40	**49** In 114 8	**50** Sn 118 7	**51** Sb 121 7	**52** Te 127 5	**53** I 126 93	.	.	**54** Xe 130.2
6 or P	**55** Cs 132.81	**56** Ba 137.36	**57–71** Rare Earths	**72** Hf 178 6	**73** Ta 181 4	**74** W 184 0	**75–Re** **186.3**	**76** Os 190 8	**77** Ir 193 1	**78** Pt 195.2
	79 Au 197 2	**80** Hg 200 6	**81** Tl 204 4	**82** Pb 207 22	**83** Bi 209 0	**84** Po 210	**85–**	... ...	.. .	**86** Nt 222.4
7 or Q	**87–** ...	**88** Ra 226 0	**89** Ac ...	**90** Th 232	**91** UX 230	**92** U 238 2	.. .	... .	.. .	... ..
Rare Earths	... ...	**57** La 138.9	**58** Ce 140 1	**59** Pr 140 9	**60** Nd 144 3	**61** Il ...	**62** Sm 150.4	**63** Eu 152 0	... ...	. ...
	64 Gd 157 3	**65** Tb 159 2	**66** Ds 162 5	**67** Ho 163 5	**68** Er 167 6	**69** Tm 169.4	**70** Yb 173 5	**71** Lu 175 0	. .	.

The Periodic Table. The periodic table of the elements is shown in the above table and it is obvious that the properties of the elements are periodic functions of their atomic numbers. After the K and L shells are completed, the next shells become more complicated and the so-called long periods follow the simple short periods. The rare gases are the key elements in the periodic table, for in these elements the outermost shells contain only completed groups of eight (helium 2). All the other elements tend to revert to these rare gas configurations. There are eight elements between helium and neon, eight between neon and argon, eighteen between argon and krypton, and eighteen between krypton and xenon. Then there are thirty-two between xenon and radon. There is a very simple and fundamental relationship between the numbers 2, 8, 18, 32, the meaning of which was

first suggested by Rydberg in 1914, and is now completely established by the determination of atomic numbers and the discovery of new elements. The maximum number of electrons which can enter the various shells is as follows:

K, 2; L, 8; M, 18; N, 32; O, 50.

The numbers actually present in the various rare gases are:

	K	L	M	N	O	P	Period	Difference	Period Length
2 Helium ..	2	..	..	..	..	..	1st	He	2
10 Neon .	2	8	..	..	..	..	2nd	Ne − He	8
18 Argon. .	2	8	8	..	..	..	3rd	A − Ne	8
36 Krypton.	2	8	18	8	..	..	4th	Kr − A	18
54 Xenon.	2	8	18	18	8	..	5th	Xe − Kr	18
86 Radon. ..	2	8	18	32	18	8	6th	Rn − Xe	32

The differences 2, 8, 8, 18, 18, 32 represent, in the earlier periods, the formation of complete or provisionally complete new shells; in the later periods they represent a combination of this process with the final completion of a group already started.

The full significance of these numerical relations is not yet apparent, but the importance of the numbers 2 and 8 are again emphasized. These numbers will be again encountered in the discussion of quantum relations in the next chapter.

Only a few of the many interesting things concerning this arrangement of the elements can be mentioned here. The rare gases with completed shells appear to be the stable configurations. Elements with only a few electrons in the outermost shells easily lose electrons and tend to simulate the rare gas of next lower atomic number, whereas elements with nearly complete rare-gas configurations tend to attach more electrons and simulate the rare gas next higher in atomic number. The former elements have metallic properties, whereas the latter elements have non-metallic properties. In sodium, where there is a tendency for the atoms to lose electrons, electrical conductance is good, but in sulphur, where each atom tends to complete its quota of eight electrons by attaching two more to complete its shell, electrons cannot migrate and the electrical conductance is very slight.

In the long periods inner groups are being reconstructed and completed, and there are various different possible electronic arrangements of nearly equal energy for each atom. Hence the positive valence is

variable. Moreover, the ions are colored when the possible electron displacements involve energy differences so small that they correspond to visible light, and the paramagnetic character of the ions is due to the presence of electrons in incomplete groups. The rare earths, the elements between titanium and copper, and the corresponding elements in the later periods show these properties. Where the atoms have the same number of valence electrons and are nearly the same size (rare-earth group) all the properties are very much alike.

Valence. It has been shown that there is a tendency for electrons to go in pairs, and a second tendency for atoms to lose or gain electrons and simulate the arrangement of electrons in the rare gases. The rule of 2 and the rule of 8 are important in building up atoms into compounds. In grouping different phenomena together under the classification of valence, it is helpful to distinguish between the various types of valence. Ferrous ions are oxidized to ferric ions and sulphite ions are oxidized to sulphate ions, but the former change involves only electrons, whereas the latter involves combination with an additional atom. The new advances in the study of valence, outlined here, are concerned chiefly with the arrangement of atoms in molecules. Three different types of interaction between atoms are recognized: (1) electrostatic attraction between ions; (2) formation of covalent linkages between atoms; and (3) intermolecular action or van der Waals' forces. There is a gradual change from one type to another and some authorities consider that all three are basically alike.

(1) Electrostatic interaction is called *electrovalence;* it involves a *transfer* of electrons, giving a *heteropolar bond.* The compounds which involve this type of valence are known as *polar compounds.* They are unsymmetrical, they have large dipole moments, and they tend to ionize. They are found chiefly among the inorganic compounds. Lithium fluoride may be cited as an example of this type. Lithium has one electron in its outermost shell and fluorine has seven. The lithium atom tends to lose its one valence electron in the outermost shell and become a lithium ion with one positive charge, and the fluorine atom tends to gain an extra electron and become a fluoride ion with one negative charge. Both tendencies are satisfied by a transfer of an electron from the lithium to the fluorine, and the rule of 2 and the rule of 8 are also followed. This electrostatic or ionic type of linkage can readily be broken apart by dissolving the compound in a medium of high dielectric constant. Lithium fluoride, for example, separates almost completely into lithium ions and fluoride ions when dissolved in water.

Other examples are given by the following equations, in which the

number of electrons in the outermost shell are indicated with dots. A completely filled shell, in the elements of low atomic number, usually has eight electrons. It is called an *octet.* Thus,

$$\mathrm{Li}\cdot + \cdot\ddot{\mathrm{F}}: = \mathrm{Li}:\ddot{\mathrm{F}}: = [\mathrm{Li}]^{+} + [\mathrm{F}]^{-}$$

$$\mathrm{Zn}:: + \ddot{\mathrm{S}}: = \mathrm{Zn}::\ddot{\mathrm{S}}: = [\mathrm{Zn}]^{++} + [\mathrm{S}]^{-}$$

$$\mathrm{H}\cdot + \cdot\ddot{\mathrm{Cl}}: = \mathrm{H}:\ddot{\mathrm{Cl}}: = [\mathrm{H}]^{+} + [\mathrm{Cl}]^{-}$$

$$\mathrm{Li}\cdot + \cdot\mathrm{H} = \mathrm{Li}:\mathrm{H} = [\mathrm{Li}]^{+} + [\mathrm{H}]^{-}$$

(2) Covalent interaction, or *covalence,* involves a *sharing* of electrons giving a *homopolar bond.* In this case the tendency to gain or lose electrons is about the same in both atoms and the two electrons are held in common between the two atoms. Compounds of this type are known as nonpolar compounds. They are more symmetrical, they have small dipole moments and little tendency to ionize. A covalent bond or homopolar bond is the same as the valence bond of organic chemistry, but it is often represented with two dots for the electron pair instead of with the straight line ordinarily used. The following equations and compounds illustrate the *covalent bond:*

$$\mathrm{H}\cdot + \cdot\mathrm{H} = \mathrm{H}:\mathrm{H}$$

$$:\ddot{\mathrm{Cl}}\cdot + \cdot\ddot{\mathrm{Cl}}: = :\ddot{\mathrm{Cl}}:\ddot{\mathrm{Cl}}:$$

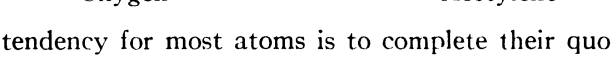
$$\begin{array}{ccc} & \mathrm{H} & \\ & \vdots & \\ \mathrm{H}:&\mathrm{C}&:\mathrm{H} \\ & \vdots & \\ & \mathrm{H} & \end{array} \qquad\qquad \begin{array}{ccc} & :\ddot{\mathrm{Cl}}: & \\ & \vdots & \\ :\ddot{\mathrm{Cl}}:&\mathrm{C}&:\ddot{\mathrm{Cl}}: \\ & \vdots & \\ & :\ddot{\mathrm{Cl}}: & \end{array}$$

Methane Carbon tetrachloride

It is interesting to note that these views of valence account satisfactorily for the fact that a hydrogen atom will combine with a negative chlorine atom, or a positive sodium atom, or with another hydrogen atom. Negative chlorine atoms combine readily with other negative chlorine atoms. These combinations were difficult to explain on the older theories of electrostatic attraction in which sodium was always considered positive and chlorine always negative. It will be observed that the new views harmonize the facts of both electrochemistry and structural organic chemistry.

Double bonds and triple bonds can be represented by the sharing of two pairs or three pairs of electrons, as shown by oxygen and acetylene. These multiple bonds seem to be possible only with atoms in the first

row of the periodic table where the outermost electrons (in the L shell) are near the K shell which contains only two electrons. The possibility of these bonds is a great aid in giving variety and complexity to organic substances.



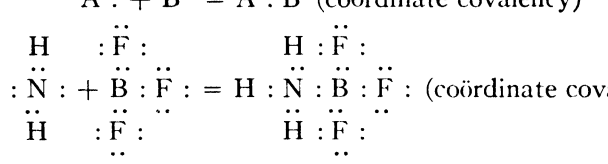
Oxygen Acetylene

The tendency for most atoms is to complete their quotas of eight outer electrons by sharing or transferring electrons, but frequently this is impossible, and an atom sometimes has only six, four or two electrons in its outer shell.

There is a special case of covalency known as *coördinate covalency* in which both electrons of the pair are contributed by the same atom instead of by the two atoms. It is illustrated in the following examples.

$$A \cdot + \cdot B = A : B \text{ (normal covalency)}$$

$$A : + B = A : B \text{ (coördinate covalency)}$$



This type of linkage is recognized in certain organic compounds.

(3) The intermolecular attraction is met with in the van der Waals' force of attraction a (p. 14) which draws gas molecules closer together and leads to the liquefaction of gases. It may involve the same forces as the electron pair, but it is not yet well understood.

Physical Properties. The difference between the electrostatic attraction and covalent attraction is quite marked.

The electrovalent or polar compounds involve simply electrostatic attraction. There is no real bond. The heat of vaporization is large and the boiling-points are high because the ions have to be separated. No isomerism is possible at a heteropolar bond because the ions are comparatively free to move around. In the crystal lattice all the forces of attraction are strong because they are between ions. The crystals are, therefore, hard and the melting-points are high.

In the covalent or nonpolar compounds the electrical forces are fairly well satisfied within the molecule and the external field is small. The crystals are soft, the melting-points and boiling-points are low, and the heats of vaporization are small. The rigid valence bonds give an opportunity for different spatial arrangements and isomerism of all types.

The coördinate bonds give properties which are midway between those of the covalent and electrovalent bonds.

Another point of interest in connection with the new theories is the prediction that compounds containing the same total number and arrangement of electrons have similar physical properties. Such compounds are called *isosteres*. Carbon dioxide and nitrous oxide each have the same number (22) of electrons arranged in the same way and are, therefore, isosteric. The freezing-points are quite different, but most of the other physical properties, including critical temperature and critical pressure, dielectric constant, viscosity, refractive index, heat conductance and surface tension, are nearly identical. The ions NO_3^- and CO_3^{--} are also isosteric, and the crystals of sodium nitrate and calcium carbonate are very similar.

Only one more relation based on these theories of valence can be mentioned here. The tendency of electrons to go in pairs is almost universal, so universal in fact that only a few molecules containing an odd number of valence electrons are known. When these odd molecules do exist, they are in fact abnormal. They tend to associate and they are usually colored. Nitrogen dioxide and triphenyl methyl are examples.

The considerations discussed in this chapter are largely qualitative. The only hope of making things more quantitative appears to be through the quantum theory, which is briefly surveyed in the following chapter.

REFERENCES

Valence and the Structure of Molecules. G. N. Lewis.
The Electron Theory of Valence. Sidgwick.
Introduction to Modern Physics, Chapters XI, XIII. Richtmeyer.
The Structure of the Atom. Andrade.
Atoms, Molecules and Quanta, Chapter II. Ruark and Urey.
Symposium on Atomic Structure, Chem. Rev., **5**, 371–603 (1928).
Periodisches System. Rabinowitsch and Thilo.

PROBLEMS

1. Give the number of protons and electrons in the nuclei of all the isotopes of (*a*) fluorine; (*b*) calcium; (*c*) iron; (*d*) sulphur.

2. Assuming the relationship $mc^2 = \epsilon = h\nu$ calculate the wave-length of the radiation emitted if 4 hydrogen atoms combine to form a helium atom.

Ans. 0.00046 Å.

3. From Aston's data it can be shown that when thorium decomposes into mesothorium and helium by the emission of an α-particle, there is a loss in weight of 0.00683 gram per gram atom of thorium decomposed. If this mass is all transformed into energy of the α-particles,

(*a*) Calculate the number of ergs of energy of each α-particle.

(*b*) To what frequency of radiation would this amount of energy correspond?

(*c*) To what wave-length?

Ans. (*a*) 1.014×10^{-5} erg. (*b*) 1.55×10^{21} per sec.

4. Write equations, illustrating electron distributions, for the formation of

(*a*) A polar compound.

(*b*) A covalent compound.

(*c*) A coördinate-covalent compound.

5. Write formulas indicating the electron distribution according to the Lewis-Langmuir concept for the following compounds:

(*a*) N_2O. (*b*) NO_2. (*c*) N_2O_3. (*d*) N_2O_5.

6. Write formulas indicating the electron distribution according to the Lewis-Langmuir concept for the following ions:

(*a*) SiO_4^{----}. (*b*) PO_4^{---}. (*c*) SO_4^{--}. (*d*) ClO_4^{-}.

7. A certain atom contains 30 positive charges and 16 negative charges in its nucleus. (*a*) Give the distribution of the outer electrons in the normal atom, (*b*) the position in the periodic system and (*c*) the name of the element.

8. Give the arrangement of the electrons in the various shells for the following elements:

(*a*) boron; (*b*) phosphorus; (*c*) calcium.

9. Look up and compare various physical properties of CO and N_2 which emphasize their isosterism.

CHAPTER XXIV

INTRODUCTION TO QUANTUM THEORY

Foundations. The great practical success of the quantum theory has led to fundamental advances in theoretical work and to a new philosophical point of view. Most of the research now being done in physics is connected with the quantum theory, and it is penetrating rapidly into chemical investigations. Although the quantum is the fundamental unit of radiation, it is intimately connected with the electron and the atom as well.

It was mentioned on p. 542 that the quantum theory was invented by Planck to help in obtaining a mathematical formula for expressing the distribution of radiation emitted by a heated solid.

Planck's formula is

$$u_\nu \, d\nu = 8\pi h \frac{\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \, d\nu, \tag{1}$$

where u_ν is the density of radiation of frequency ν, c is the velocity of light, k is the gas constant per molecule (R/N) called the Boltzmann constant, and h is a constant now known as Planck's constant. In arriving at this formula, Planck was led to discard the classical wave theory of light in favor of this new arbitrary hypothesis that light is emitted and absorbed in units which he called quanta, and that the energy of a quantum is directly proportional to the frequency of the light. This proportionality constant h has turned out to be a very important universal constant.

Formula (1) can be integrated to give the Stefan-Boltzmann law (p. 540); it approaches the Rayleigh law (p. 541) as ν approaches zero, and it approaches the Wien distribution law (p. 541) as ν approaches infinity. Moreover, it is in agreement with the Wien displacement law. Planck's radiation formula then is in remarkable agreement with the various facts of radiation and it gives experimental values with excellent precision. In spite of these successes the formula would probably have failed to obtain general acceptance on account of the radically new assumption concerning quanta, except for the fact that almost at once it became extremely useful in new and

unrelated fields. Its importance in photochemistry has been discussed. It has revolutionized the study of spectroscopy. Critical potentials, photoelectric effects and specific heats have all been interpreted quantitatively with the help of the quantum theory.

According to the classical theories of specific heats there is an *equipartition of energy* among the different atoms in a molecule. The molar heat capacity at constant volume is $\frac{3}{2} R$ (p. 29) for monatomic gases, and there are three possible directions and three degrees of freedom in the translational energy. Each degree of freedom then has associated with it $\frac{1}{3} \times \frac{3}{2} R = 1$ calorie per degree. For each extra atom in the molecule there are more degrees of freedom and a greater heat capacity. Actually, however, the polyatomic gases have heat capacities which are much less than those calculated on the basis of the number of degrees of freedom. Also, there is nothing in the classical theory to lead one to expect the large temperature coefficient of heat capacity which is actually found. Furthermore, diatomic hydrogen gas at low temperatures has a molar heat capacity of 3 calories and behaves exactly as a monatomic gas. Again, on the classical theory, crystals of solid elements should have a heat capacity of 6 calories per degree (p. 83), but a few crystals like carbon, and in fact all crystals at sufficiently low temperatures, have a heat capacity much smaller than 6. Apparently some of the degrees of freedom are "frozen up" at the lower temperatures. The restricting of the degrees of freedom found an explanation in the quantum theory of restricted energy units, and formulas involving the quantum, $h\nu$, were applied, with considerable success, to specific heats at low temperatures.

There seems, then, to be adequate experimental justification in many fields for the quantum theory, according to which radiation is composed of units called quanta, and the energy of each quantum ϵ is given by the equation (page 542)

$$\epsilon = h\nu \tag{2}$$

where h has the value 6.547×10^{-27} erg-second and ν is the frequency of the radiation in reciprocal centimeters. In many applications of the quantum theory certain restrictions and arbitrary quantum numbers are introduced which appear as integers in the various formulas.

Spectroscopy. The quantum theory has had its greatest success in the interpretation of spectra, and the pioneer work is due to Bohr. In 1913, Bohr* proposed the fundamental hypothesis that electrons exist in definite energy levels, E_1, E_2, etc., without emitting or absorbing radiation, but that when an electron changes from one level to

* Phil. Mag., **26**, 1, 476, 857 (1913).

another, monochromatic radiation is emitted or absorbed in accordance with the following equation:

$$E_2 - E_1 = \epsilon = h\nu. \tag{3}$$

Bohr assumed that the electrons revolve around the nucleus in elliptical orbits, and that the centrifugal force is equal to the force of electrostatic attraction. In accordance with the new ideas he assumed further that the motion of the electron was *quantized*, and that instead of an infinite number of possible orbits there is only a restricted number with properties represented by functions of the quantum number n, where n is an integer 1, 2, 3, 4, $\cdots$. By a simple application of mechanics and electrodynamics he showed that the energy E_n in a particular orbit n is

$$E_n = \frac{-m(Ze)^2e^2\,4\,\pi^2}{2\,n^2h^2}, \tag{4}$$

where m is the mass of the electron, Z is the atomic number, e is the charge on the electron, h is Planck's constant, and n is an integer. Then according to equation (2) the quantum of light emitted on changing from one orbit to another is given by the formula

$$\epsilon = h\nu = E_{n_2} - E_{n_1} = \frac{2\,\pi^2me^4Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). \tag{5}$$

Several of these quantities can be grouped together giving a constant known as the Rydberg constant R, defined as follows:

$$R = \frac{2\,\pi^2me^4}{h^3c}. \tag{6}$$

Then substituting into equation (5), for hydrogen with an atomic number of 1,

$$\tilde{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \tag{7}$$

where R_H has the value 109,677.76 and $\tilde{\nu}$ refers to wave-numbers.*

* The different ways of expressing radiation (pp. 99 and 538) are reviewed in the following equations:

λ = wave-length. 1 Å = 0.1 mμ = 10^{-7} mm. = 10^{-8} cm.

c = velocity of light = $\lambda\nu$ = 3×10^{10} cm. per sec.

ν = frequency = $\dfrac{3 \times 10^{10}}{\lambda_{\text{cm.}}}$.

$\tilde{\nu}$ = wave-number = $\dfrac{1}{\lambda_{\text{cm.}}}$.

$\nu = (3 \times 10^{10})\tilde{\nu}$

For example, green light of 5000 Å or 5×10^{-5} cm. has a frequency of $\dfrac{3 \times 10^{10}}{5 \times 10^{-5}} = 6.0 \times 10^{14}$, and a wave-number of $\dfrac{1}{5 \times 10^{-5}} = 20{,}000$.

Now the visible lines in the spectrum of hydrogen had been measured accurately and Balmer, in 1885, pointed out that they could be represented by an empirical formula equivalent to the following:

$$\tilde{\nu} = A\left(\frac{1}{2^2} - \frac{1}{n_2{}^2}\right) \tag{8}$$

where n_2 is a whole number greater than 2 and A is a constant. It is obvious that equation (7) is the same as equation (8) and that it constitutes an excellent check on the theoretical calculations. In fact the numerical value of R, expressed in eight significant figures, was obtained from spectral measurements rather than from equation (6), because some of the constants in the latter equation are known only to one part in a thousand.

It will be noticed in equation (8) that n_2 cannot be less than 2 for then $\tilde{\nu}$ would be a meaningless negative number, and that it cannot be 2 for then $\tilde{\nu}$ becomes zero. As n_2 becomes larger than 2 the corresponding value of $\tilde{\nu}$ becomes larger, but when n_2 is already large further increases cause $\tilde{\nu}$ to increase only very slightly, and as n_2 approaches infinity $\tilde{\nu}$ approaches $\frac{1}{4} R_H$.

A few of the lines of the Balmer series as calculated by equation (7) setting $n_1 = 2$ are given in the following table.

BALMER LINES IN THE HYDROGEN SPECTRUM

n_2	$\tilde{\nu}_{calc.}$	$\mathring{A}_{calc.}$	$\mathring{A}_{obs.}$
3	15,233.22	6,562.79	6,562.8
4	20,564.79	4,861.33	4,861.3
5	23,032.54	4,340.47	4,340.5
6	24,373.07	4,101.74	4,101.7
7	x	y	. . . .

The success of the Balmer formula led to further exploration and Lyman found another series in the ultra-violet spectrum of hydrogen which is just as satisfactorily represented by formula (7), provided n_1 is given the value 1 instead of the value 2 as in the Balmer series, but n_2 then has values 2, 3, 4, etc. The lines calculated from this formula are known as the Lyman series. The Paschen series occurs in the infra-red, and these lines are accurately reproduced by formula (7) when $n_1 = 3$ and n_2 has values greater than 3. These series are represented diagrammatically in Fig. 170. Light is emitted when the electron returns from a level of high energy (large quantum number) to a level of lower energy.

The intimate connection between these energy levels and the actual lines in the spectrum may be seen by comparing Fig. 170 with Fig. 171, which is adapted from an ultra-violet spectrogram of a star by R. H. Curtiss. The same sequence of lines is observed, converging to a limit. A much larger number of lines (35) has been observed in certain stars than in laboratory experiments because the gas pressures are low and there is more room for the large "orbits."

The continuous emission beyond the convergence limit of the lines shown in Fig. 171 is always present and it is particularly significant. In the region where sharp lines are obtained definite quantum restrictions are involved, but when the electron comes in from an indefinitely great

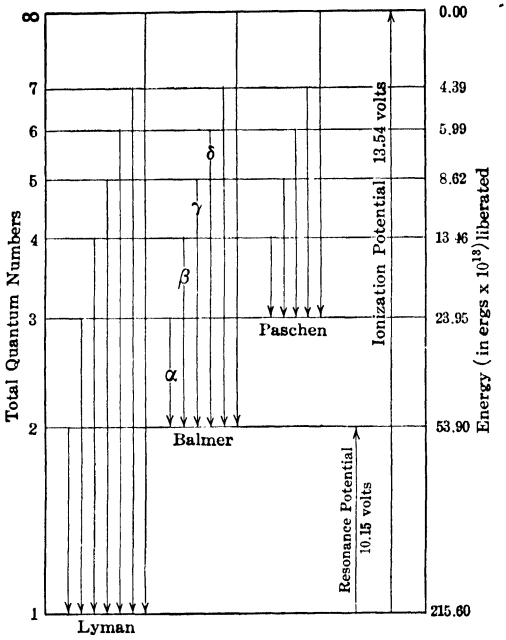


FIG. 170

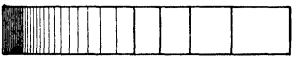


FIG. 171

distance the electron can bring with it unquantized kinetic energy which can vary continuously in magnitude and thus it can give a continuous range of frequencies. The convergence limit in the spectral series corresponds then to complete separation of the electron, i.e., to ionization. In this discussion the emission of light has been emphasized, but the absorption mechanism is the same except that the electrons are driven out to levels of higher energy by the absorption of quanta of energy, whereas in emission they fall back to levels of lower energy.

Similar formulas have been developed for helium and the alkali metals and other elements involving a single valence electron. Each element has a slightly different value of the Rydberg constant R. It is necessary to apply correcting terms which become smaller as the quantum numbers become larger.

Bohr's formula was so successful in calculating the lines of the hydrogen spectrum with exactness that the model on which it was based

was generally accepted. The elliptical orbits seemed perfectly natural by analogy with the orbits of the planets, but of course it does not follow that because a mechanism gives results which agree with experimental facts the mechanism is proved. Still other mechanisms may give the same results.* In this particular case the quantum numbers are important but they do not have to come necessarily from elliptical orbits. In fact a more complicated mathematical model based on wave mechanics has now been devised which works just as well in predicting the positions of the lines, and, in addition, it gives the intensities of the lines and it applies also to the elements heavier than hydrogen. The elliptical orbits then, like the cubical atoms, are not to be taken literally.

Quantum Numbers. The spectrum of atomic hydrogen can be splendidly interpreted by the simple Bohr formula making use of two numbers. Other spectra are much more complicated and more quantum numbers are needed in calculating the spectral lines. It is found that many spectral lines have fine structure and with sufficient dispersion give doublets, triplets, etc. Furthermore, the lines are affected by a strong electrostatic field giving the *Stark effect* and by a magnetic field giving the *Zeeman effect*. In the more complex spectra some of the lines can be grouped together in overlapping series depending on their Stark and Zeeman effects and on their general appearance. Thus, one series of lines is characterized by having particularly sharp lines and another by having diffuse lines. Several characteristic types of spectra have come to be recognized by spectroscopists, and are called the principal (*p*), sharp (*s*), diffuse (*d*) and fundamental (*f*), etc.

Now all these variations can be handled by using four arbitrary quantum numbers. These numbers and their symbols are as follows:

n = principal quantum number.

when n =	1	2	3	4	5
the corresponding symbols are	K	L	M	N	O

l = subordinate quantum number.

when l =	0	1	2	3
the corresponding symbols are	*s*	*p*	*d*	*f*

m = magnetic quantum number.

m depends on l and may have any integral value between $+l$ and $-l$. Therefore, $2l + 1$ values of m are possible.

$\boldsymbol{s}$ = electron spin number.†

Two values of $\boldsymbol{s}$ are possible corresponding to two possible directions of rotation. Since the quantum numbers can vary only by integers, $\boldsymbol{s}$ can have only the values $-\frac{1}{2}$ and $+\frac{1}{2}$.

* Mathematicians are not really satisfied with the solution of a problem until they have proved that it is the only possible solution, but chemists are too inclined to be satisfied with the first solution that works.

† This $\boldsymbol{s}$ for spin number is not to be confused with *s* for sharp series.

The various combinations of the three quantum numbers n, l and m, permitted by the restrictions given above, are recorded in the following table:

POSSIBLE COMBINATIONS OF PRINCIPAL, SUBORDINATE AND MAGNETIC QUANTUM NUMBERS

n	Group	l	Sub-group	m
1	(K)	0	(s)	0
2	(L)	0	(s)	0
2	(L)	1	(p)	−1 0 +1
3	(M)	0	(s)	0
3	(M)	1	(p)	−1 0 +1
3	(M)	2	(d)	−2 −1 0 +1 +2
4	(N)	0	(s)	0
4	(N)	1	(p)	−1 0 +1
4	(N)	2	(d)	−2 −1 0 +1 +2
4	(N)	3	(f)	−3 −2 −1 0 +1 +2 +3

The number of figures in column m gives the number of possible combinations, but this number must be doubled because for each of these figures two values of the spin number ($-\frac{1}{2}$ and $+\frac{1}{2}$) are possible. For example in an s state where $l = 0$, m can have only the value 0 and s can have the value $+\frac{1}{2}$ or $-\frac{1}{2}$. There are then two possible combinations. In a p state where $l = 1$ there can be 3×2 possible combinations; in a d state where $l = 2$ there can be 5×2 combinations; and in an f state, 14 possible combinations.

It seems natural that four quantum numbers should be necessary to describe the motion of an electron, three coördinates for its location in space and a fourth number which is attributed to the spin of the electron around its own axis. The recognition of these four quantum numbers has been a great aid in understanding many physical and chemical phenomena particularly through the application of the restriction now to be described.

Pauli's Exclusion Principle. According to Pauli* *two electrons in a single atom can never have all four quantum numbers the same.* This principle is a great help in explaining the missing lines in spectra, and the number of elements in the different groups of the periodic table.

The K, L, M and N shells in the various atoms have the principal

* Z. Physik **31**, 765 (1925).

quantum numbers 1, 2, 3 and 4, and the subordinate quantum numbers must be at least one number less. The K shell can have only the *s* sub-group, the L shell can have only *s* and *p* sub-groups; the M shell can have *s*, *p* and *d* sub-groups; and the N shell can have *s*, *p*, *d* and *f* sub-groups. It has just been seen that there are two possible combinations for an *s* state, and hence by Pauli's principle only two different kinds of atoms are possible. For the *p* state there can be six, and so on. Summing up the total number of different possible combinations, each combination giving rise to one and only one kind of atom, we have:

K shell with *s* sub-group gives 2 atoms.
L shell with *s* and *p* sub-groups gives $2 + 6 = 8$ atoms.
M shell with *s*, *p* and *d* sub-groups gives $2 + 6 + 10 = 18$ atoms.
N shell with *s*, *p*, *d* and *f* sub-groups gives $2 + 6 + 10 + 14 = 32$ atoms.

This sequence 2, 8, 18, 32 is exactly the sequence which was found empirically in the preceding chapter. Furthermore, the order in which the succeeding sub-shells are filled up as the atomic number increases accounts for some of the characteristics of the periodic table.

The further application of these quantum numbers to describe complicated spectra is beyond the scope of this book.* It may be stated, however, that the capital letters *S*, *P*, *D* and *F* are used to designate atomic states rather than single electron states and that superscripts before a letter refer to the number of sub-levels in the state, giving doublets, triplets, etc. Spectral lines are of course described by the difference between two terms, designating the quantum numbers of the two energy levels. For example, the strong ultra-violet line of mercury at 3663 Å is described in quantum symbols as $2^3P_2 - 3^1D_2$.

Critical Potentials. Further insight into the structure of atoms can be obtained by measuring the voltage necessary to give a free electron sufficient energy to activate or ionize an atom or molecule. Again the quantum theory is the guiding principle because the energy changes are quantized. It is not possible to have an infinite number of energy changes between energy states, but only a few definite changes, and these bear a definite relation to the spectral lines. The free electrons must have certain velocities in order to react with a given molecule, just as light must have certain frequencies in order to be absorbed by it. The energies of the electrons must be sufficient to correspond to

* Further material is given in a simple manner in "Quantum Chemistry," by Haas, and Chem. Rev., **5**, 109 (1928) by Dushman.

definite energy transitions in the molecule or there can be no interaction. This is a fundamental postulate of the quantum theory.

The apparatus shown in Fig. 172 is a simple one which permits the direct experimental measurement of critical potentials. A filament is heated to emit electrons, and an adjustable potential V_1 of several volts is applied between it and the grid G_1, the latter being charged positively. When the tube is thoroughly evacuated the electrons coming from the filament are driven through the grid and across the tube to the plate P, whence they pass through the galvanometer to the ground. An opposing potential V_3 is increased until the electrons are barely able to reach the plate. A trace of gas, mercury vapor for example, is next admitted, and the slow-moving electrons suffer many elastic collisions with the molecules without loss of energy and they still reach the plate and are registered by the galvanometer. As the potential V_1 is increased gradually, the current through the galvanometer increases approximately as the three-halves power of the voltage. Eventually, however, the current decreases suddenly because the electrons have acquired sufficient kinetic energy to cause a definite displacement of electrons from one energy level to a higher energy level, in the molecules composing the gas. This effect is due to inelastic collisions in which the energy of the moving electron is consumed by the molecule, and the colliding electrons then retain insufficient velocity to reach the plate. As the potential is increased still further, the electrons acquire more energy, some of which is retained after collision. The subsequent collisions of these electrons with other molecules again become elastic and the electrons reach the plate and register an increased current through the galvanometer.

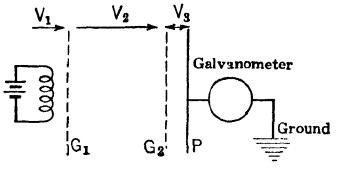


FIG. 172

This process is continued as the potential is gradually increased, and several peaks corresponding to definite energy changes are recorded. A curve of this type, in which electron current is plotted against the voltage, is shown in Fig. 173, where Einsporn's data* on mercury vapor are

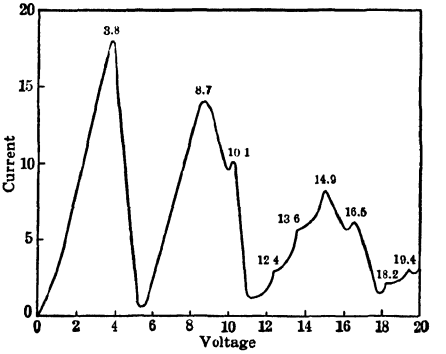


FIG. 173

* Z. Physik, 5, 208 (1921).

given. The critical potentials are taken as the voltages at which the current first starts to decrease, but it is necessary to apply a correction to all the values shown in Fig. 173 because the electrons leave the filament with a definite kinetic energy, in this case amounting to 1.1 volt. The first critical potential then is 4.9 rather than 3.8.

The second grid G_2 and reversible potentials V_2 and V_3 are designed to distinguish between the two kinds of critical potentials, namely, ionization potentials and resonance potentials.* Since V_2 is small the collisions will occur in a weak electrical field.

An *ionization potential* is a potential which gives to a free electron sufficient energy to ionize the molecule, i.e., to drive the valence electron completely out of the molecule leaving a positive ion. *Resonance potentials* are potentials sufficiently great to cause the emission of light when the free electrons collide with molecules. They involve the displacement of valence electrons to higher energy levels and their return to lower energy levels with the emission of light in accordance with equation (2). Less energy is required for displacement than for separation, and for a given substance the resonance potentials are less than the ionization potential. The resonance potentials correspond to activated states and should play a part eventually in the problem of chemical reaction.

There is an obvious and simple relation between the electrical energy, the kinetic energy and the radiation energy involved in these quantum changes, as given by the following equation:

$$V'e = \tfrac{1}{2} mv^2 = h\nu, \tag{9}$$

where e is the charge on the electron, m its mass and v its velocity, and V' is the potential drop through which the electron falls. The latter is expressed in electrostatic units; it may be converted into ordinary volts V by multiplying by the factor 300. Then referring to p. 602,

$$\frac{Ve}{300} = h\nu = hc\tilde{\nu} = Rhc\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{10}$$

or

$$V = \frac{300\,Rhc}{e}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{11}$$

where n_1 and n_2 are the quantum numbers 1, 2, 3, 4, 5, etc.

This equation is used in the following table to show the numerical relation between spectral lines and critical potentials in the Lyman series of atomic hydrogen, where $n_1 = 1$. The critical potentials were measured at high temperatures where the hydrogen molecules are largely dissociated. The constant $300\,Rhc/e$ has the value of 13.539.

* Davis and Goucher, Phys. Rev., **10**, 101 (1917).

COMPARISON OF SPECTRAL LINES AND CRITICAL POTENTIALS

Quantum Number n_2	Wave-length Å obs.	Wave-number Å obs.	Volts $V_{calc.}$	Volts $V_{obs.}$
2	1215	82,258	10.154	10.15
3	1026	97,491	12.034	12.05
4	973	102,823	12.692	12.70
5	950	105,291	12.997	13.00
6	938	106,631	z	.....
7	931	107,440	13.262	13.27
∞	912	109,678	13.539	13.54

The agreement between the calculated and observed voltages is excellent, again strengthening the underlying quantum theory on which the calculations are based. In many cases it is possible to show the actual emission of light of the expected frequency by bombarding with electrons of the proper voltage, new lines being brought in as the voltage is increased.

Electron velocities and even spectral quantities are often expressed in terms of volts, calculated with the help of equation (9). The term volt when applied to energy quantities really means electron-volt.

Photoelectric Effect. We have seen that light quanta can be emitted by bombardment with electrons, and it is to be expected that electrons can be emitted by bombardment with quanta of light. In 1887, Hertz discovered that when a spark-gap is exposed to ultra-violet radiation, the voltage necessary for the passage of a spark is appreciably lowered. It was found that this effect was due to the emission of electrons, and the consequent ionization of the air between the terminals of the spark-gap.

The phenomenon was subsequently further investigated by Hallwachs* who found that when the surface of a charged piece of zinc was illuminated by ultra-violet light it lost the electric charge which it possessed. He also showed that an insulated piece of zinc acquired a positive charge when exposed to ultra-violet light, owing to the emission of electrons. This phenomenon, which has since been found to be quite general, is known as the *photoelectric effect.*

This interesting effect has been utilized in the photoelectric cell, which is probably the most sensitive instrument yet devised for the detection and measurement of radiation. A diagram of such a cell is shown in Fig. 174. A film of metallic potassium K is deposited *in vacuo* on the lower half of the inner surface of the tube T. A platinum

* Hallwachs, Wied. Ann., **33**, 301 (1888).

wire serves to connect this film with the negative terminal of a 300-volt battery B, while the other terminal of the battery is connected through a sensitive galvanometer, or electrometer, G, with the platinum wire W. When the upper half of the tube is exposed to incident radiation, the potassium emits electrons which are attracted to the positively charged wire W, and thus a current is set up which produces a deflection in the galvanometer proportional to the intensity of the illumination.

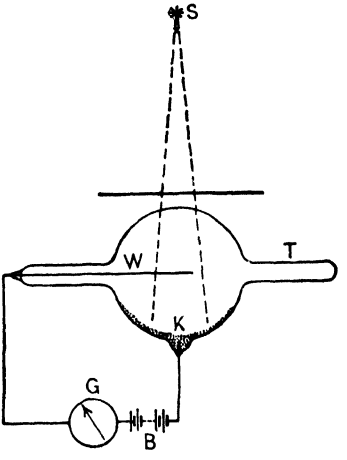


FIG. 174

According to the quantum theory,* the energy of photoelectrons varies directly with the frequency of the radiation, according to the equation,

$$\tfrac{1}{2}mv^2 = Ve = h\nu - h\nu_0, \qquad (12)$$

where m and v denote the mass and velocity of the electrons, respectively; V, the potential difference necessary to retard the velocity of the electron to zero; e, the electronic charge; ν, the frequency of the incident radiation; ν_0, the limiting frequency (sometimes termed the "photoelectric threshold"); and h, Planck's constant. In equation (12), $h\nu$ measures the energy absorbed by the electron from the incident radiation; $h\nu_0$ represents the energy consumed in bringing the electron to the surface of the metal, and $\frac{1}{2}mv^2$ is the actual kinetic energy of the emergent electron. This latter magnitude is measured by the product Ve. A number of different metals have been examined by Millikan† with a view to testing the validity of equation (12) and, within the limits of experimental error, he has found that for any photoelectrically active surface, the maximum value of V increases linearly with the frequency, ν, of the incident radiation, the slope of the curve being given by the ratio of h to e. In fact, the experimental determination of this slope offers an excellent method for evaluating the constant h.

It should be emphasized that the *velocity* of the ejected electrons depends on the frequency of the light, and that the *number* of electrons ejected per second depends on the intensity of light, i.e., the number of quanta striking the surface per second.

The current in a photoelectric cell can be readily amplified with the

* Einstein, Ann. Physik, **17**, 132 (1905); **20**, 199 (1906).

† J. Franklin Inst., **184**, 337 (1917).

aid of an ordinary electron tube to operate a relay, and the photoelectric cell is now finding many important applications* in automatic controls, safety devices and laboratory appliances, as well as in television and "sound-pictures."

The Compton Effect. The photoelectric effect involves the complete absorption of a quantum, but it is possible also for a quantum to impart only a portion of its energy to an electron. This transfer of energy, giving the electron an accelerated velocity and reducing the frequency of the quantum, is known as the *Compton effect*. The phenomenon may be expressed by the following equation, in which ν_0 is greater than ν,

$$h\nu_0 + \text{electron} = h\nu + \text{electron with greater momentum.} \quad (13)$$

Compton† bombarded carbon and other light elements with short X-rays and found, with the help of a crystal lattice and spectrometer, that part of the scattered radiation had a shorter wave-length than the incident radiation.

This fundamental experiment, together with the realization that any physical measurement involves interaction with the measuring instruments, led Heisenberg‡ through mathematical considerations to the *principle of uncertainty*. According to this principle it will never be possible to know with exactness *both* the position and the momentum of an electron or other small particle. It is not a matter of physical imperfections in the measuring apparatus but a fundamental limit of nature, according to which (the error of measuring position) × (the error of measuring momentum) is approximately equal to Planck's constant, h. The position of a small particle can be known with exactness but then its velocity is uncertain, and in the same way the momentum can be known only at the sacrifice of exact information regarding its position.

The principle is of no importance in ordinary work because the particles involved are so large that the uncertainty is utterly negligible. It does have an important bearing on philosophy,§ however, for heretofore it had been supposed that there was no theoretical limit imposed on science.

Raman Effect. A quantum of radiation may undergo elastic collision with a molecule, in which case the scattered light has the same frequency as the incident light. It may be completely absorbed, as

* Daniels, Mathews, and Williams, "Experimental Physical Chemistry," p. 432. "The Photoelectric Cell," General Electric Bulletin.

† Phys. Rev., **21**, 483 (1923).

‡ Z. Physik, **43**, 172 (1927).

§ Bridgman, "The Logic of Modern Physics."

explained on earlier pages, or it may contribute part of its energy to displacements of the atoms in the molecule. These atomic displacements are quantized; i.e., only certain displacements are possible corresponding to definite energy increments or simple functions of these increments. Each of these quantized atomic displacements gives rise to absorption in the infra-red portion of the spectrum.

The *Raman effect* involves the collision of a quantum with a molecule, under conditions such that there is an interchange of energy, giving scattered radiation of slightly different frequency from that of the incident radiation, and a change in the energy of atomic oscillation. Such a collision of a quantum with a molecule may then be represented by the equation

$$h\nu_0 = h\nu_{\text{Raman}} \pm h\nu_{\text{infra-red}}, \tag{14}$$

where ν_0 is the frequency of the incident light and ν_{Raman} is the frequency of the scattered light, the difference being numerically equal to $h\nu_{\text{infra-red}}$, which may correspond to a characteristic infra-red frequency. Usually ν_{Raman} is smaller than ν_0 because the quantum imparts some of its energy to the molecule. The wave-length of the reflected light is then longer than that of the incident light, in accordance with Stokes' law of fluorescent spectra. It is possible, however, for a quantum of incident radiation to absorb a small infra-red quantum from a molecule and leave with greater energy. In this case ν_{Raman} is greater than ν_0, and the lines are called anti-Stokes lines. They are weaker than the Stokes lines because the transfer of a small quantum to a large quantum is less probable.

Although the Raman lines may correspond to infra-red absorption lines, they can correspond to transitions which are improbable by the restrictions of the quantum theory; i. e., to frequencies which do not occur in the ordinary absorption spectrum. Valuable information concerning the structure of a molecule can thus be obtained from both the Raman and the absorption spectra.

Although this effect had been predicted by the quantum theory, it remained for Raman* in 1928 to demonstrate that the scattered light does actually contain radiation of different frequency. The difficulty lay merely in giving long enough exposure to detect the feeble Raman lines which tend to be obliterated by light of the exciting frequency. The material is placed in front of a spectrograph slit and illuminated transversely with a mercury vapor lamp, preferably with light filters, for many hours as shown in Fig. 175. In Fig. 176 the Raman spectrum of quartz, adapted from a photograph by Pringsheim, is clearly

* Indian J. Phys., **2**, 387 (1928).

shown. On each side of the exciting line are seen lines which correspond to the infra-red absorption lines indicated.

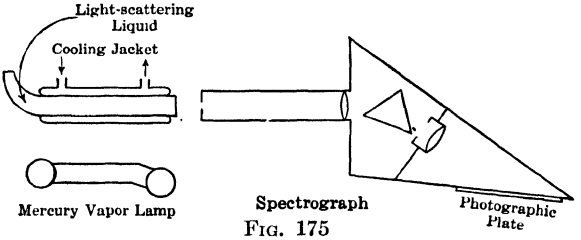
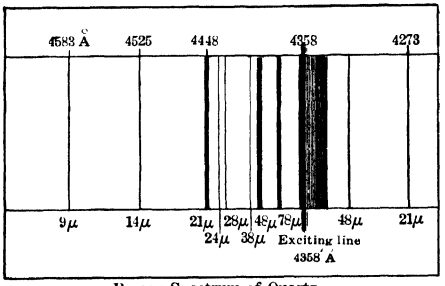


FIG. 175

Within the three years following the announcement of Raman's discovery nearly five hundred papers on this subject have been published and material of considerable importance in physical chemistry has been accumulated.*



Raman Spectrum of Quartz under influence of Mercury Line at 4358 Å (Pringsheim)

FIG. 176

Quantum Collisions. The collisions between quanta and molecules are particularly important in photochemistry. Several possibilities are indicated in the following summary:

A quantum plus a molecule may give:

1. Quantum + molecule (no reaction).
2. Quantum of different frequency + molecule with displaced atoms (Raman effect).
3. Quantum of lower frequency + electron with increased velocity (Compton effect).
4. $Atom_1$ + $atom_2$ (dissociation).
5. $Atom_1$ + excited $atom_2$ (dissociation + excitation).
6. Electron + positive ion (ionization).
7. Excited molecules (excitation).

The excitations may be followed by:

(*a*) Return to normal condition with emission of radiation (fluorescence).
(*b*) Collision with another molecule giving increased kinetic energy, i.e., rise in temperature.
(*c*) Collision with another molecule and decomposition of the latter.
(*d*) Collision with another molecule and combination of the two.
(*e*) Collision with a second molecule and formation of a complex molecule followed by dissociation into new products.

* The following review articles are recommended: Dadieu and Kohlrausch, J. Optical Soc., **21**, 286 (1931); Andrews, J. Chem. Education, **8**, 1133 (1931).

Examples of most of these phenomena are found among various photochemical reactions, some of which have already been mentioned in an earlier chapter. There is a fundamental distinction in absorption spectra between excitation phenomena and dissociation phenomena. Absorption spectra are discontinuous when the molecules are excited because the absorption is governed by definite quantum restrictions. However, when a molecule is dissociated, giving either normal atoms, excited atoms or ions, the fragments are given a certain amount of kinetic energy which is not quantized. Accordingly, when the energy becomes great enough (the wave-lengths become short enough) to cause dissociation, the absorption becomes continuous. These phenomena are indicated in Fig. 177, where typical discrete lines corresponding to excitation are sketched at the right, heading into a band of continuous absorption at the left, corresponding to dissociation. The numbers refer to quantum numbers in the band spectrum. Just as the long wave-length limit of continuous absorption in Fig. 171 permitted calculation of the energy of ionization of hydrogen atoms, so also the long wave-length limit of continuous absorption in band spectra permits a calculation of the energy of dissociation of the molecule.

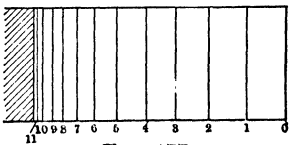


FIG. 177

In a few cases the discrete lines become very hazy below a definite wave-length. This phenomenon is known as *pre-dissociation* and the energy of dissociation can be calculated from the hazy line of longest wave-length.

It is possible then to make important calculations and predictions in photochemistry from the type of absorption spectrum.* For example, hydriodic acid is dissociated directly by ultra-violet light in the region where continuous absorption exists. Einstein's law holds and one molecule is decomposed for each quantum absorbed because there are no secondary reactions. Bromine and hydrogen combine when radiated with light in the region of discontinuous absorption by bromine, and one concludes then that this reaction involves collisions with activated bromine molecules. Norrish† has reported that nitrogen dioxide in the region of discontinuous absorption shows fluorescence, as described under 7(*a*), at low pressures where molecular collisions are few; and it decomposes, as described under 7(*c*), at higher pressures when activated molecules collide with unactivated molecules.

* The photochemical significance of different types of spectra together with specific examples is fully discussed by Taylor, J. Phys. Chem., **34**, 2049 (1930), and "Treatise on Physical Chemistry," Chapter XVIII.

† J. Chem. Soc., 761 (1927).

Band Spectroscopy. So many important quantities, including heats of dissociation, specific heats, entropies, atomic vibrations, internuclear distances, intermediate compounds and isotopes, can now be calculated from band spectra that a further discussion seems justified, although a quantitative treatment is beyond the scope of this book. Absorption in the far infra-red (50 μ to 100 μ, for example) involves small quantities of energy, due to rotation of the molecule. Even here the energy absorption is quantized and only certain quantities of

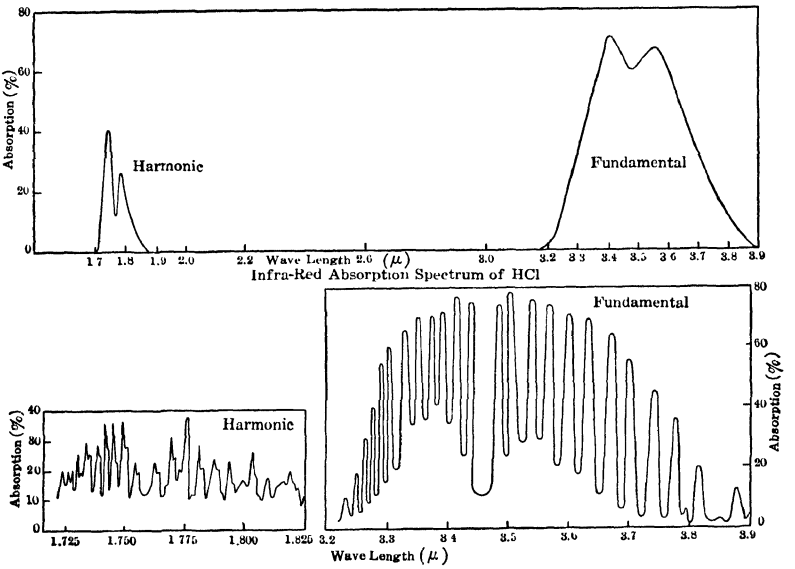


FIG. 178

energy can be absorbed, but the difference between them is very small. In the near infra-red (1 μ to 50 μ) there is absorption by the displacement of atoms within the molecule, and the rotation spectrum is superimposed on the vibration spectrum giving simple bands in the short infra-red, such as are shown in Fig. 178* for hydrochloric acid.

A diatomic molecule may be likened to a dumb-bell, and Rayleigh showed that a rotating-vibrating molecule of this type having an electric moment should emit and absorb light of frequencies $\nu_v \pm \nu_r$, where ν_v is the frequency of vibration and ν_r is the frequency of rotation. When $\nu_r = 0$, the absorption is slight, and a series of absorption lines is obtained by adding terms with quantum numbers of rotation 1, 2, 3, 4, etc., and a second series of lines is obtained by subtracting them.

* Adapted from Brinsmade and Kemble, Proc. Nat. Acad. Sci., **3**, 420 (1917); and Jones, Astrophys. J., **50**, 251 (1919).

These two branches have maxima as indicated in Fig. 178. The distance between these maxima permits a calculation of the distance between the atomic nuclei in the molecule.

The bands recur at definite intervals (1.75 μ and 3.7 μ in HCl) which are governed by the integer multiples so common in quantum phenomena, except that small correcting terms, owing to secondary phenomena, are usually necessary. Under high dispersion the fine structure of the bands due to the quantized rotation of the molecule is apparent, as shown in the inserts in Fig. 178.

In one of the inserts it will be noted that the saw-teeth of the band are irregular, a hump occurring on the long wave-length side of the high peaks. This is a clear demonstration of the existence of isotopes, HCl^{37} having a slower rate of vibration than HCl^{35}. There is more of chlorine^{35} than of chlorine^{37} in ordinary chlorine, and so its absorption is greater.

These rotation-vibration spectra are often superimposed, with some distortion, on spectra due to electron displacements, giving band spectra in the visible and ultra violet. The band of the compound CN, at 4216 Å is sketched in Fig. 179. Combinations of these three factors — rotation, oscillation, and electronic displacement — give very complex spectra, but in many cases they have been adequately interpreted. The description of various types and the notation of band spectra have been developed by Mulliken.*

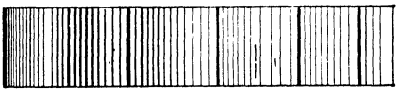


FIG. 179

The lines, owing to rotational transitions, come closer and closer together, indicating the head of a band, and all the bands connected with a single electron transition constitute a *band system*. All the band systems of all the electrons taken together constitute the *band spectrum*. The analysis of band spectra offers a powerful means for identifying materials present, either in emission spectra or absorption spectra. The molecules giving rise to emission spectra do not necessarily correspond to ordinary valence types of molecules, as for example in the case of BH, O_2, O_2^+, CN, BO, etc. Molecules with thirteen electrons, BeF, BO and CN, are particularly simple, for each atom has two electrons in the K shell and a stable octet is then formed leaving one extra electron, which resembles in this way the simple spectra of hydrogen and the alkali metals. A molecule with fourteen electrons, such as CO, has two extra electrons and its spectrum resembles, to a certain extent, the spectra of the alkaline-earth metals such as calcium. Mole-

* Chem. Rev., **6**, 503 (1929).

cules of MgF, AlO and SiN have twenty-one electrons in all, four in the K shells, then two groups of eight, and then an extra electron, so that those compounds again resemble the alkali metals in their spectra.

The interpretation of band spectra offers now the most sensitive test for isotopes. Giauque and Johnson,* by careful examination of the sun's spectrum photographed through the many kilometers of air which surround the earth, discovered isotopes of oxygen having masses of 17 and 18. By a quantitative examination of the spectrum of CN, King and Birge were able to show that all the lines could be accounted for only on the assumption of an isotope of carbon with a mass of 13 together with ordinary carbon of mass 12.

Energy of Dissociation. It has been pointed out that the energy required to dissociate a molecule can be calculated from the convergence limit of the heads of the bands in the band spectrum, and the beginning of continuous absorption. In such calculations it is customary to express the spectra in terms of volts, and it is convenient to remember that

$$1000\ \text{Å} = 12.34 \text{ volts (electron-volts)},$$

and

$$1 \text{ volt} = 23{,}060 \text{ calories per mol.}$$

Since the energy varies directly as the frequency and inversely as the wave-length, 2000 Å corresponds to 6.17 volts, and xÅ corresponds to $12.34 \times 1000/x$ volts, where x is any number.

These calculations may be illustrated in the case of chlorine, which dissociates into one normal atom and one excited atom as indicated under 5 on p. 614. The continuous absorption, beginning at the convergence of the bands, occurs at 4785 Å corresponding to 2.577 volts. The extra energy of excitation of the atom corresponds to 0.109 volt, as determined spectroscopically. The difference, 2.468 volts, gives at once the energy required to disrupt the molecule. It corresponds to 56,900 calories, whereas direct thermal measurements give of 57,000.

Further information regarding dissociation energies can be obtained from diagrams like that shown in Fig. 180, where the potential energy is plotted against the distance between atomic nuclei.† Some atoms like helium repel each other at all distances; the potential energy is greatest when the atoms are close together and it falls off gradually to zero, as shown by the upper curve. More often the atomic nuclei repel each other at very close distances and attract each other at large distances, but the attraction becomes less as the distance becomes very

* J. Am. Chem. Soc., **51**, 1436, 3528 (1929).

† Franck, Z. Physik, **31**, 411 (1925).

great. This situation is represented by the lower curve in Fig. 180; it is obvious that there must be a minimum somewhere in the potential energy curve. This minimum corresponds to the most stable condition of the molecule, and although the atoms oscillate back and forth in the molecule they tend to keep this distance corresponding to the minimum point. The energy required to dissociate the molecule can be calculated from this curve, if one knows the potential energy when the atoms are at infinite distance apart and when they are at this stable point. The exact shapes of the curves ordinarily are not known but sometimes they can be obtained empirically from the data of band spectroscopy.

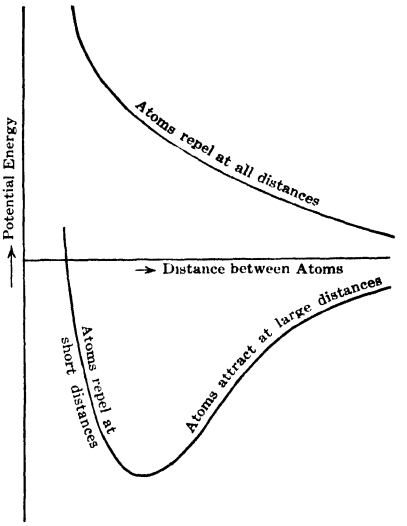


FIG. 180

New Quantum Mechanics. The quantum theory is largely a theory of restrictions, and these restrictions have been determined empirically from laboratory measurements. Considerable attention was paid, therefore, to finding a theoretical foundation for these restrictions; Heisenberg and Born devised a theory based on matrix calculus and probabilities; De Broglie and Schrödinger developed a theory based on differential equations applied to waves; and Dirac embraced both in general terms with a new system of mathematics. Heisenberg's treatment and Schrödinger's treatment are both aspects of the same underlying principle, and, from both, the restrictions of the quantum theory come out automatically as mathematical necessities.

The Schrödinger wave equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad (15)$$

where m = mass of particle, $V_{x,y,z}$ is its potential energy in a field of force, and E is its total energy, a constant. The quantity ψ is called the "wave function" because in many problems it exhibits a wave-like series of maxima and minima. Where $|\psi|^2$ is large, there is a large concentration of electrons; in general, $|\psi|^2$ determines the probability of an electron being in a specified region. ψ is determined by solving the differential equation (15), when sufficient information is available.

The fundamental postulate is that the wave function must be continuous, single-valued and finite throughout all space. Solutions which meet these requirements are possible only when E is given certain characteristic values (Eigenwerte), and the corresponding solutions of ψ are called characteristic solutions (Eigenfunctions).

These characteristic values give the stationary states of the Bohr theory, and thus the quantized energy levels result automatically from the Schrödinger wave equation.

The new quantum mechanics is much superior to the older theories because, in addition to accomplishing all that they accomplished, it solves more complicated problems and gives in many cases better agreement with experiment. Only three of the many successful applications of the new quantum mechanics can be mentioned here.

On the basis of the wave equations, electrons as well as radiation may be considered as waves, and the wave-length of an electron is given by the simple formula

$$\lambda = \frac{h}{mv} = \frac{12.2}{V^{\frac{1}{2}}} \text{ Å}, \tag{16}$$

where V is the potential difference in volts under which the electron is travelling. Davisson and Germer* showed, in 1925, that streams of electrons do have properties attributed to waves and like X-rays may be refracted by a single crystal. The wave-lengths agree with those calculated from equation (16). There is evidence also that hydrogen atoms or protons have certain properties of waves and give diffraction patterns with a crystal lattice. It appears then that matter, electricity and radiation are composed of discrete particles — atoms, electrons and quanta. However, in all these cases a group of these particles taken together may exhibit the properties of waves.

The pairing of electrons which has been stressed in the last two chapters is explained on the basis of the new theory. An electron pair consists of two electrons which are identical in their quantum states, except that their spins are in opposite directions. This idea has led to new and very promising views of valence.†

One of the most striking achievements of the new theories was the prediction that hydrogen should exist in two different forms, which are now called ortho- and para-hydrogen. It was predicted that eigenfunctions of diatomic molecules with like nuclei can be either

* Proc. Nat. Acad., **14**, 317, 619 (1928).

† Heitler and London, Z. physik. Chem., **44**, 55 (1927); London, Z. physik. Chem., **46**, 455 (1928); Slater, Phys. Rev., **37**, 481 (1930); Pauling, J. Am. Chem. Soc., **53**, 1367 (1931).

symmetric or anti-symmetric, depending on the spins of the nuclei. Experimental evidence for the two forms was found in band spectra, where alternate lines were missing or very weak, and in the abnormal specific heats of hydrogen at low pressures.

Bonhoeffer and Harteck* succeeded in separating these two forms and in demonstrating the difference in specific heat and other properties. At room temperature ordinary hydrogen is a mixture of three parts of ortho-hydrogen (antisymmetric type) and one part of para-hydrogen (symmetric type); at the temperature of liquid air the equilibrium is 1 to 1, and at the temperature of liquid hydrogen the ortho-hydrogen is not stable and goes entirely into the para- or symmetric form, when catalyzed with charcoal.

REFERENCES

Quantum Chemistry. Haas.
J. Chem. Education, **8**, 1074–1113 (1931), Dushman.
J. Chem. Education, **8**, 1114–1132 (1931), Urey.
Treatise on Physical Chemistry, Chapter XVI. Taylor. (Dushman.)
Treatise on Physical Chemistry, Chapter XVIII. Taylor.
Atoms, Molecules and Quanta. Ruark and Urey.
Chem Rev., **7**, 467–507 (1928). Van Vleck.
Chem. Rev., **10**, October (1931). Rodebush.

PROBLEMS

1. From equation (4) calculate the energy of the hydrogen atom in the normal state ($n = 1$). *Ans.* 2.153×10^{-11} erg.

2. Calculate the value of the Rydberg constant for hydrogen and compare with the experimental value.

3. Calculate the values of x and y in the table on p. 603.

4. Calculate ν, $\tilde{\nu}$ and λ for the line in the Paschen series of the hydrogen spectrum which is due to a transition from the fourth quantum level to the third.

5. There is a Brackett series in the hydrogen spectrum where $n_1 = 4$. Calculate the wave-lengths, in Ångstrom units, of the first two lines of this series.

6. According to the Heitler and London theory of valence, chemical combination takes place between atoms possessing equivalent electrons (that is, electrons otherwise alike but which differ in their spin quantum numbers), whose spins compensate one another as the valence bond is formed, the electrons forming a "pair." Within an atom, the spins of two electrons may also compensate each other; the pair thus formed is inactive toward chemical combination. With the help of these considerations and the Pauli exclusion principle, the observed valency of the first row elements may be reproduced. Thus oxygen, with 2 electrons in the first sub-group and 4 in the second sub-group of the valence shell, may have a valence of 0 or 2, since

n	2	2
l	0	1
m	0	$-1, 0, +1$

* Z. physik. Chem., **43**, 113 (1929).

Six electrons of suitable spins must fit into four positions; these can go $+\frac{1}{2}$, $-\frac{1}{2}$; $+\frac{1}{2}$, $-\frac{1}{2}$; $+\frac{1}{2}$, $-\frac{1}{2}$; for which all are paired and the valence is zero, or $+\frac{1}{2}$, $-\frac{1}{2}$; $+\frac{1}{2}$, $-\frac{1}{2}$; $+\frac{1}{2}$; $+\frac{1}{2}$, in which two are unpaired and the valence is two. Find in the same way the valence of

(*a*) fluorine and of (*b*) carbon.

7. Add 1.1 volt to values given in Fig. 173 and determine some of the peaks by simple combinations of the two fundamental resonance potentials 4.9 and 6.7. For example, $2 \times 4.9 = 9.8$ and $4.9 + 6.7 = 11.6$.

8. Calculate the velocity of a cathode particle which has been accelerated by a potential of 100 volts. *Ans.* 5.95×10^8 cm. sec^{-1}.

9. Calculate the value of the constant $\frac{300\,Rhc}{e}$ for hydrogen.

10. Calculate the value of z in the table on p. 610.

11. Show that the energy of a quantum of wave-length 1000 Å corresponds to that of a 12.34 volt electron.

12. Calculate the number of calories per mol corresponding to one "volt" of energy.

13. (*a*) To what voltage does the infra-red line at 10 μ correspond?

(*b*) What wave-length corresponds to an energy of 1 volt?

14. (*a*) To what voltage does the ultra-violet line of mercury at 3663 Å correspond?

(*b*) A quantum of what wave-length has the same energy as a seven-volt electron?

15. (*a*) Express X-radiation of 0.1 Å in terms of volts.

(*b*) Express energy of 100,000 volts in terms of wave-length.

16. From the observed values of the critical potentials of hydrogen in the table on p. 610 calculate

(*a*) The wave-length of the first two lines of the Lyman series.

(*b*) The wave-length of the first line of the Paschen series.

17. What is the energy in volts of an α-particle having a velocity of 1.5×10^9 cm. sec.$^{-1}$? *Ans.* 2,335,000 volts.

18. An experiment on the emission of photoelectrons from a sodium surface gave the following values for the potentials at which the photoelectric current was reduced to zero:

(Å)	V (volts)
5461	−2.045
4339	−1.488
4047	−1.295
3651	−0.914
3125	−0.382
2535	+0.52

Plot frequency against voltage and determine Planck's constant from the slope of the line.

19. Calculate the wave-lengths of the Raman lines (Stokes and anti-Stokes) which are produced by the combination of the infra-red absorption of quartz at 21 μ with an exciting line of wave-length 4358 Å. Compare with the observed values in Fig. 176.

20. What are the wave-lengths of the Raman lines produced by combining the absorption frequency of quartz at 48 μ with exciting light having a wave-length of 4358 Å?

21. According to the hypothesis of Franck, the molecules of the halogens dissociate into one normal atom and one excited atom. The wave-length of the convergence limit in the spectrum of iodine is 4995 A.

(*a*) What is the energy of dissociation of iodine into one normal and one excited atom?

(*b*) The lowest excitation energy of the iodine atom is 0.94 volt. What is the energy corresponding to this excitation?

(*c*) Compute the heat of dissociation of the iodine molecule into two normal atoms, and compare it with the value obtained from thermochemical data, 34.5 Cal. per mol.

Ans. (*a*) 56.96 Cal.

22. Assuming the DeBroglie relation, that the wave-length associated with a particle is equal to Planck's constant divided by the momentum, derive equation (16).

23. What is the wave-length of electrons which have fallen through a potential of (*a*) 400 volts? (*b*) 1000 volts? *Ans.* (*a*) 0.61 Å.

INDEX OF AUTHORS

A

Adair, 218
Adams, 178, 179, 286
Adkins, 286
Adler, 495
Adriani, 310
Alexander, 210, 243
Alexejeff, 143, 145
Allmand, 452, 481, 504
Amagat, 11, 14
Andrade, 595
Andrews, 33, 614
Ångström, 99, 344
Aristotle, 2
Arrhenius, 194, 196, 197, 198, 199, 201, 205, 338, 380, 381, 382
Aston, 392, 561, 565, 566, 570, 591
Avogadro, 3, 5, 6, 15, 19, 20, 29, 106, 193, 195, 205, 213, 214, 215, 243, 275, 345, 365, 546, 562, 563, 580

B

Bäckstrom, 477
Balmer, 603
Baly, 100, 104, 108
Bancroft, 232, 243, 317
Barry, 259
Beattie, 452, 458
Beccaria, 360
Bechhold, 225
Beckmann, 171, 177
Becquerel, 572
Beer, 544
Bein, 458
Bennett, 494
Bergmann, 267
Berkeley, 167, 184, 185, 188
Bernoulli, 22
Berthelot, 37, 38, 133, 246, 259, 267, 268, 284
Berzelius, 3, 360
Bhatnagar, 233
Bigelow, 171, 356
Biilmann, 473
Biltz, 226, 227
Bingham, 52, 58, 60
Birge, 618
Bjerrum, 415, 452
Blagden, 174
Blasdale, 317
Bodenstein, 275, 276, 329, 355
Böhi, 415, 464
Bohr, 601, 602, 604, 605, 620
Boltwood, 5, 580
Boltzmann, 22, 106, 341, 540, 600
Bonhoeffer, 551, 621
Born, 619
Böttger, 393, 465
Boyle, 2, 9, 13, 14, 24, 33, 183
Brackett, 621
Bragg, 71, 73, 77, 85
Bray, 353, 354, 409, 576
Bredig, 228, 229, 380, 414
Brewer, 584
Bridgman, 300, 612
Brinsmade, 616
Britton, 242
Brockman, 504
Brönsted, 354, 479
Brown, 212, 213, 215, 231
Brühl, 92, 94
Brumbaugh, 452
Budde, 13
Bunsen, 25, 141, 500, 548
Burk, 350
Burnham, 494
Burton, 167, 211
Butler, 134
Byers, 494

C

Cady, 43
Cailletet, 48, 49
Cameron, 590
Cannizzaro, 3

Carlisle, 360
Carnot, 125, 128
Carroll, 173
Chadwick, 586, 588
Clapeyron, 128, 129, 168, 175, 281, 299
Clark, 85, 463, 470, 471, 481
Claude, 41, 42, 44
Clausius, 22, 124, 129, 168, 175
Clément, 27
Compton, 612, 614
Coolidge, 78, 382, 557
Coombs, 55
Cornu, 101
Corran, 452
Coster, 570
Cottrell, 173, 174, 232
Cotton, 220
Coulomb, 391, 478
Craft, 348
Craig, 498
Creighton, 397, 504
Crookes, 557
Crowther, 570
Curie, 5, 573, 581
Curtiss, 604.
Cushman, 452

D

Dadieu, 614
Dalton, 1, 2, 3, 46, 139, 140, 142, 290, 294
Daniell, 421, 428
Darrow, 570
Davey, 79
Davies, 397
Davis, 259, 609
Davisson, 616, 620
Davy, 360
Debierne, 25
Debray, 288
De Broglie, 619
Debye, 77, 81, 82, 106, 108, 199, 201, 477, 478, 516, 526
Denham, 414, 472
Desch, 104, 159, 317
Desormes, 27
Deville, 19
Dewar, 41, 171
Dirac, 619
Dobbie, 104
Dole, 475, 477, 480
Draper, 233
Duane, 568
Dufford, 542
Dulong, 3, 82, 540
Du Noüy, 56, 60
Dunstan, 60
Dushmann, 607, 621
Dutoit, 392, 395
Dutrochet, 180

E

Edison, 499
Einsporn, 608
Einstein, 216, 526, 545, 548, 550, 551, 611, 615
Elbs, 504
Elliott, 225
Ellis, 452, 553, 586
Eötvös, 55
Essex, 452
Eucken, 525
Evans, 391, 542
Eyring, 323

F

Fajans, 581, 586
Fales, 469
Falk, 194, 371, 376
Falkenhagen, 480
Faraday, 40, 97, 105, 363, 364, 365, 421, 487, 494
Faure, 497
Fenwick, 475, 477
Findlay, 191, 317
Fink, 397, 504
Finkle, 233
Fletcher, 215
Forbes, 548
Fowler, 532
Fraenkel, 414
Franck, 618
Franklin, 405
Fraunhofer, 539
Frazer, 165, 188, 242, 353
Fresnel, 544
Freudenberg, 495
Freundlich, 222, 223, 239, 240, 242, 243, 244

Friedel, 348
Friedrich, 68
Fuchs, 489
Furman, 418, 474
Fuson, 89

G

Gay-Lussac, 9, 24, 115, 183
Geibel, 395
Geiger, 579, 580
Gelbach, 452
Geoffrey, 267
Germer, 620
Getman, 54, 202, 390, 452, 517, 522
Giauque, 618
Gibbons, 390
Gibbs, 7, 131, 133, 236, 237, 238, 281, 297, 429, 430, 508
Gibson, 83, 525
Glasstone, 397
Goodwin, 459
Gortner, 243
Goucher, 609
Gouy, 212
Graham, 25, 208, 209, 223
Gray, 576, 577
Grotthuss, 545
Grübe, 481
Grüters, 395
Guggenheim, 456, 457
Guldberg, 49, 269, 288
Gulliver, 317
Guthrie, 306
Guye, 49

H

Haas, 607, 621
Haber, 350, 351, 501
Hall, 405, 477
Hallwachs, 610
Hammet, 418
Hampson, 40, 41
Hardy, 223
Harkins, 56, 522, 590
Harned, 452, 469, 521
Hart, 452
Harteck, 621
Hartley, 104, 105, 167, 184, 185, 188
Hasche, 329
Hatshek, 243
Hautefeuille, 275
Heisenberg, 612, 619
Heitler, 620, 621
Helmholtz, 111, 133, 281, 429, 430,444, 508
Henri, 108
Henry, 141, 142, 145, 146, 162, 163, 253, 293, 294, 512
Hertz, 610
Hess, 248, 249, 261
Heuse, 167
Hevesy, 570
Heycock, 317
Heydweiller, 392, 415
Hildebrand, 53, 160, 191, 233, 465, 466, 469
Hill, 319
Hinshelwood, 134, 339, 340, 350, 357
Hirn, 111
Hitchcock, 516
Hittorf, 367, 371
Hofmeister, 236
Hollaender, 553
Hopkins, 570
Horsch, 452, 517
Horstmann, 291
Hostetter, 477
Hückel, 199, 201, 477, 478, 516
Hudson, 415
Hulett, 155, 286
Hull, 77, 78, 79

I

Isambert, 289, 291, 292
Itano, 396

J

Jahn, 382, 458
Jeans, 596
Jensen, 477
Jobling, 357
Johnson, 618
Johnston, 323, 336
Jones, 202, 203, 351, 374, 616
Josephs, 374
Joule, 111, 115, 116, 117

K

Kahlenberg, 382, 477
Kanolt, 415
Kekulé, 94
Kelley, 528
Kemble, 616
Kendall, 349
Kenney, 228
Kharasch, 260
King, 618
Kirchhoff, 47, 257, 539, 540
Kistiakowsky, 553
Knipping, 68
Knobel, 452
Koelichen, 402
Kohlrausch, 373, 376, 378, 380, 386, 392, 393, 395, 415, 480, 614
Kolthoff, 395, 396, 418, 474, 481
Konowalow, 148
Kopp, 19, 86, 87, 88, 92
Kraemer, 233, 243
Kraus, 397, 405
Kroenig, 22
Kruyt, 210, 243
Kundt, 28
Kunz, 438
Küster, 395

L

Lamb, 353, 455, 456
Lambert, 102, 543
La Mer, 479, 522
Landolt, 95, 108
Langbein, 259
Langmuir, 241, 242, 244, 591
Laplace, 28, 248
Larson, 455, 456
Latimer, 525
Laue, 68, 71
Lavoisier, 247
Le Bas, 87, 108
Le Blanc, 488, 491, 492, 497
Le Chatelier, 133, 134, 157, 158, 277, 299, 351
Le Clanche, 504
Lehmann, 84, 85
Leighton, 548
Lemoine, 275
Lenard, 555
Lewis & Randall, 134, 200, 255, 256, 284, 431, 452, 479, 481, 506, 512, 515, 517, 519, 520, 531, 532
Lewis, G. N., 83, 131, 200, 201, 273, 284, 452, 454, 456, 480, 511, 521, 525, 530, 591, 598
Lewis, W. C. McC., 344
Ley, 414
Lind, 585, 586
Linde, 40, 41, 42
Lindeman, 525
Linder, 217, 218, 219
Linhart, 452, 521
Livingston, 354, 355
Löb, 504
Loeb, 31
London, 620, 621
Loomis, 452
Lorentz, 92, 106
Lorenz, 92, 106, 389, 415, 464
Lovelace, 165
Lubs, 470
Lucasse, 452
Lummer, 540
Lumsden, 18
Lunden, 415
Lyman, 603

M

MacDougall, 134, 481, 532
MacInnes, 386, 452, 454, 456, 458, 475, 477, 495
MacLaurin, 168
Macleod, 89
Mathews, 50, 107, 171, 173, 221, 264, 553, 586, 612
Mathias, 48, 49
Maxwell, 22, 339, 340
Mayer, 26, 111, 248
McBain, 242
McKeown, 452
Meacham, 452
Mellor, 284, 317, 357
Mendeleeff, 5
Meyer, 15, 16, 18, 31, 446
Millard, 370, 371
Miller, 64, 65, 70

Millikan, 5, 215, 538, 561, 562, 590, 591, 611
Milner, 478
Ming Chow, 452
Mitscherlich, 3, 67
Moore, 44
Morgan, 56
Morley, 16
Morse, 181, 184, 188
Mortimer, 457
Moseley, 568, 570
Mouton, 220
Müller, 477
Muller, 553
Mulliken, 617
Myrick, 188

N

Natterer, 13
Nernst, 19, 52, 288, 293, 294, 355, 391, 443, 445, 452, 458, 525, 528, 529, 536
Neville, 317
Newbery, 495
Newman, 397
Newton, 3, 267
Nicholson, 360
Nicol, 66, 94, 95, 103, 104
Nollet, 180
Nordlund, 215
Norrish, 351, 615
Noyes, 194, 371, 376, 382, 387, 415, 452, 478
Nutting, 103

O

Ohm, 361, 384, 422, 574
Onnes, 42
Ostwald, 55, 86, 182, 236, 245, 347, 394, 400

P

Paliatseas, 104
Palitzsch, 470
Palmaer, 444
Paneth, 586
Parker, 452
Parks, 525, 528
Partington, 134, 264
Paschen, 603
Pasteur, 97
Patrick, 242, 329
Pauli, 606, 607
Pauling, 620
Pearce, 452, 457
Perkin, 98
Perrin, 5, 212, 213, 215, 216, 221, 558
Peters, 438
Petit, 3, 82, 83, 540
Pfeffer, 182, 183, 184
Philip, 142, 202
Pickering, 231
Picton, 217, 218, 219
Planck, 5, 6, 542, 546, 600, 611, 612
Planté, 497
Plateau, 232
Plotnikow, 553
Poggendorf, 422
Poiseuille, 57, 59
Polack, 452
Popoff, 438
Prideaux, 417, 418
Pringsheim, 540, 613
Prout, 3, 566, 587
Pulfrich, 90

Q

Quincke, 232

R

Rabinowitsch, 598
Raman, 612, 613, 614
Ramsay, 47, 50, 55, 56, 140, 576, 577
Randall, 452, 517, 522, 532
Randall (See Lewis & Randall)
Rankine, 47, 343
Raleigh, 165, 541, 542
Raoult, 162, 163, 164, 168, 174, 176, 188, 190, 511
Rayleigh, 540, 541, 600, 616
Read, 174
Redgrove, 260
Reed, 326
Regnault, 15
Reicher, 328
Reinders, 310
Reinitzer, 84
Reuss, 219, 221
Rice, 357

Richards, 5, 55, 247, 259, 447, 514, 525
Richtmyer, 570, 598
Rideal, 243, 357, 358
Roberts, 330, 475, 477
Roberts-Austen, 159
Robertson, 522
Robinson, 160
Rodebush, 621
Roebuck, 118
Roentgen, 566, 572
Roginsky, 229
Rollefson, 173
Roozeboom, 306, 531
Roscoe, 153, 548
Roseveare, 326
Royds, 576
Ruark, 598, 621
Rutherford, 5, 575, 576, 579, 580, 585, 586, 588
Rydberg, 594, 602, 604

S

Sabatier, 351, 352
Salm, 417
Sameshima, 513
Sargeant, 454, 456
Scatchard, 202, 452, 522
Schenck, 317
Scherrer, 77
Schilling, 264
Schlesinger, 389
Schmidt, 146, 147
Schoeffel, 553
Scholnikoff, 229
Schottky, 532
Schreinemakers, 312, 313
Schreiner, 452
Schrödinger, 619, 620
Schulze, 222
Semenoff, 356
Senderens, 351
Senier, 2
Sheppard, 220, 225
Sher, 260
Shields, 55, 56, 414, 415
Sidgwick, 599
Siedentopf, 210
Slater, 620
Smiles, 108
Smith, 242
Smyth, 106
Snell, 89
Soddy, 565, 568, 581, 583, 586
Sörensen, 218, 463, 464, 470
Spoehr, 553
St. Gilles, 268, 279
Stamm, 233
Stark, 605
Stas, 3
Steele, 386
Steenbock, 553
Stefan, 540, 600
Steno, 65
Stokes, 215, 218, 243, 560, 613
Storch, 528, 535
Strickler, 221
Style, 553
Sugden, 89, 108
Summer, 546
Svedberg, 213, 218, 219, 227, 229, 243
Swietoslawski, 92, 260

T

Tammann, 300
Taylor, 286, 357, 553, 615
Taylor's Treatise, 31, 264, 284, 317, 349, 357, 397, 418, 431, 481, 521, 532, 551, 553, 586, 615, 621
Than, 20
Theriault, 326
Thilo, 599
Thilorier, 40
Thole, 60
Thompson, 397, 504
Thomsen, 259, 264
Thomson, 116, 117, 391, 557, 558, 559, 563
Thornton, 259
Tolman, 338, 357
Traube, 180
Travis, 228
Trouton, 51, 52
Tutton, 85
Tyndall, 210, 211

U

Urbain, 543
Urey, 599, 621

V

Van der Waals, 13, 14, 34, 35, 36, 37, 42, 52, 87, 142, 185, 199, 595
Van't Hoff, 140, 158, 159, 183, 184, 193, 284, 295, 296, 338
Vanselow, 522
Van Suchtelen, 396
Van Vleck, 621
Verhoek, 510
Vierordt, 180
Vinal, 504
Volta, 360, 421
Von Babo, 162
Von Weimarn, 233
Vosburgh, 498

W

Waage, 269, 288
Walden, 387, 391
Walker, 48, 328
Walpole, 470
Ware, 243, 469
Washburn, 167, 174, 370, 371, 374, 458
Watson, 52
Weigert, 551
Weiser, 234
Weiss, 63
Wells, 553
Welsbach, 353
Wenzel, 267
Westgren, 215
Weston, 425, 426
Wheatstone, 374
Whetham, 385, 386
White, 264
Wien, 541, 542, 600
Wiener, 212
Willard, 477
Williams, 106, 107, 257, 264, 480, 553, 586, 612
Williamson, 348
Wilson, 585
Winninghoff, 409
Wood, 543
Wörmann, 263
Wüllner, 162
Wright, 311
Wyckoff, 79, 85

Y

Yeh, 456
Young, 37, 46, 47, 50, 60, 156, 160, 356

Z

Zeeman, 605
Zsigmondy, 210, 211, 225

INDEX OF SUBJECTS*

A

Absorption, 538, 543
  coefficient, 102
  and constitution, 104
  of light, 98, 544
  spectrum, 98
  tube, Baly's, 100
Acids, basicity of, 394
  polybasic, 401
Actinometer, 548
Activation, energy of, 338
Active and passive molecules, 337
Activities, 273, 510
  of acetone-ether solutions, 513
  from electromotive force, 514
  of cadmium chloride, 517
  from freezing-points, 520
  of H ions, 464
  and ionic strength, 479
  of N_2O_4 and NO_2, 510
  of solvent from solute, 518
  of thallium amalgams, 514, 519
  from vapor pressures, 512
Activity, 448
  coefficients, 449, 451
  at infinite dilution, 450
  coefficient, sodium chloride, 521
Activity, mean, 449
Addition, in kinetics, 349
Additive property, 86
Adiabatic calorimeter, 247
  expansion, 121
Adsorption, 238, 349
  exchange, 240
  isotherm, 239
  theory of, 241
After-effect, 549
Alloys, 313
Alpha (α), 381, 448
Alpha particles, counting, 579
  rays, 575
Amorphous, 62
Ampere, 361
Ångström, 99, 602
Anions, 364
Anisotropic, 65
Anode, 364
Associated liquids, 256
Association in solution, 193
Atoms, 2
Atom, weight of single, 5
Atomic heats, 3
  heat capacity, 83
  nuclei, structure of, 589
  number, 571, 591
  number, even, 590
  numbers, from X-rays, 566
  structure, 588
  weights, 3
  weights, table of, 4
Auto-catalyst, 349
Avogadro's constant, 5, 365, 562
  constant from radioactivity data, 580
Average life, 578

B

Balmer series, 603
Band spectroscopy, 616
Basicity of organic acids, 393
Beta rays, 575
Bimolecular reaction, 326, 331
  reaction mechanism, 344
Biological applications of photochemistry, 552
Boiling-point apparatus, Cottrell, 173
  change in, 131
  constant, 170
  and critical temperature, 49
  elevation of, 167
  experimental determination of, 170
Brass, 496
Bridge, salt, 427, 455

*Arranged for review as well as for reference.

Brownian movement, 212
Buffer action, 470
  solutions, 469
  solutions, standard, 471

C

Cadmium cell, 425
Calculus, 109
Calomel cell, normal, 427
Calorie, large, 245
  small, 245
Calorimeters, 246
  Parr's, 248
Capacity factor, 110
Capillary rise and surface tension, 53
Carbon dioxide isothermals, 33
Carbon monoxide removal, 353
Carnot's cycle, 125
Catalysis, 347
  applications of, 351
  bromine-bromide, 354
  contact, 349
Catalyst, 347
Catalytic reactions in solution, 354
Cataphoresis, 219
Cathode, 364, 556
  particle, charge, 560
  particle, velocity of, 559
  potential, 502
  rays, 557
Cations, 364
Cell constant, 375
Cells, reversible, 428
  without transference, 457
Chain reactions, 355, 550
Chemical energy and electrical energy, 428
  equilibrium and temperature, 281
Chemiluminescence, 542
Cloud track method, 585
Cobaltammines, 479
Colligative properties, 86
Collisions, frequency of, 342
  of quanta, 614
  with surface, 342
Colloids, 208
  condensation methods, 228
  dispersion methods, 228
Colloids, nomenclature, 209
  particle, weight of, 218
  precipitation of, 221
  preparation of, 227
  preparation of, by arc method, 229
  solutions, physical properties, 216
Common ion effect, 410
Compton effect, 612
Concentration cells, 446
  cell, silver nitrate, 448, 454
  cells with transference, 453
  cells without transference, 456
Concentration, volume, 138
  weight, 138
Conductance cells, 374
  measurements, application of, 392
  of different substances, 375
  electrical, 360, 362
  of electricity through gases, 554
  equivalent, 372, 377
  equivalent at infinite dilution, 378
  of fused salts, 388
  ionic, 376, 380
  ionic at infinite dilution, 378
  and ionization, 380
  molar, 372
  of non-aqueous solutions, 389
  of pure liquids, 387
  ratio, 449, 382
  of silver nitrate in different solvents, 390
  of solutions of sodium chloride, 373
  specific, 372
  of strong electrolytes, 376
  of sulphuric acid, 388
  temperature coefficient, 386
  viscosity correction, 383
  of water, 392
  of weak electrolytes, 376
Conductimetric titrations, 396
Conjugate phases, 312
Continuity of gaseous and liquid states, 34
Consecutive reactions, 334
Constitutive property, 86
Conventions in sign of E.M.F., 431
Cooling curve, 314
Corresponding states, 37
Cosmic radiation, 538, 590
Coulomb, 361

Coulometers, 366
silver, 366
titration, 366
volume, 366
weight, 366
Counter reactions, 333
Covalence, 596
Critical point, 312
Critical potentials, 607
potentials and spectral lines, 610
Critical solution temperature, 145
Critical temperature, 55
Cryohydrate, 304
Crystal angles, 65
form and chemical composition, 67
notation, 64
structure of cubical, 69
structure of sodium chloride, 73
Crystals, properties of, 65
Crystalline, 62
Crystallography, 63
Crystalloids, 208
Current concentration, 487
density, 487
efficiency, 487
Cubic atom, 591
Cycle, 120

D

Decomposition potential, 488, 491
potentials of HCl, 492
ΔF, 132, 507
ΔH, 113, 245, 509
ΔU, 112
Density of colloids, 217
Depolarization, 490, 500
Depolarizers, 500, 502
Derivative, 109
Dialysis, 223
Dielectric constants, 105, 107
Differential, 109
Diffuse series, 605
Dipole moments, 105
Disintegration series, radioelements, 580, 582
Disperse systems, 208
Displacement of particles, 215
Dissociation ammonium carbamate, 291
Dissociation of ammonium hydrosulphide, 291
of calcium carbonate, 289
of carbon dioxide, 278
constant, 278
constants of N_2O_4, 283
degree of, 196, 381
energy of, 618
of gases, 20
heat from equilibrium, 282
of hydrates of copper sulphate, 292
of hydriodic acid, 275
of nitrogen pentoxide, 324, 336
of nitrogen tetroxide, 21, 276
of phosphorous pentachloride, 277
in solution, 193
theory of complete, 198
of water, 392
Distillation of binary mixtures, 149
fractional, 150
steam, 155
Distribution of benzoic acid, 295
coefficient, 294
of energy, 541
of a solute, 293
of succinic acid, 294
Dropping electrode of mercury, 445
Dry cell, 504

E

e, 364
Edison battery, 499
Eigenfunctions, 620
Einstein, 546
Electrode, bimetallic, 477
calomel, 427
gas, 461
glass, 475
hydrogen, 427, 461
irreversible, 428
normal hydrogen, 427
null, 426
overvoltages, 495
oxide, 474
potential single, 431
quinhydrone, 473
reaction, 442
reference, 426
unpolarizable, 490

Electroendosmosis, 220
Electric charge, 562
Electrical conductance, 381
  conductance determination, 373
  conductance history, 360
  theory of matter, 556
  units, 361
Electroluminescence, 543
Electrolysis, 364, 487, 500
  electron theory of, 365
Electrolytes, classification of, 200
  mixture of two, 406
  osmotic properties of, 201
Electrolytic cells, 487
  dissociation, theory of, 195
  equilibrium, 400
  oxidation, 503
  reduction, 501
  separation, 495
  solution pressure, 443
Electromagnetic unit, 362
Electrometric determination of valence, 460
Electromotive force, 421
  and chemical equilibria, 435
  applications of, 456
  of concentration cells, 447
  measurement, 422
  signs, 431, 435
  of polarization, 488
Electron, 216
  charge on, 562
  pair, 598
  shells, 594
  spin, 605
Electroplating, 496
Electrostatic unit, 362
Electrovalence, 595
Emission, 539
Emulsification, oriented wedge theory of, 233
Emulsifier, 231
Emulsifying agent, 231
Emulsions, 231
End points by conductance, 395
  points, graphical method for, 476
Energy, 110
  efficiency, 487
  kinetic, 110
Engine, mercury, 127
Entropy, 522
  change with temperature, 523
  chemical equilibria from, 528
  and free energy, 527
  of perfect gas, 524
  tables of, 527
Enzymes, 353
Equation (see also *formula, law*)
  of Arrhenius (ionization), 338, 381
  of Berthelot (gases), 37
  of Boltzmann (statistical), 341
  of Clapeyron (vaporization), 128
  of Clausius-Clapeyron (vaporization), 129
  of Einstein (colloid displacement), 216
  of Einstein (photochemistry), 545
  of Freundlich (adsorption), 239
  of Gibbs-Helmholtz (free energy), 429, 430
  of Langmuir (adsorption), 241
  of Nernst (electrode), 443
  of Planck (radiation), 542
  of Schrödinger (wave mechanics), 619
  of van der Waals (gases), 13, 34, 37
  of van't Hoff (equilibria), 284, 338
Equilibrium acetic acid and alcohol, 268, 280
  constants, 269
  in gaseous systems, 275
  in liquid systems, 279
Equipartition of energy, 601
Equivalent conductance, 372, 377, 480
Etch figures, 66
Eutectic mixture, 317
  point, 317
Exclusion principle, Pauli, 606
Experiments of Perrin, 213
Explosions, 356
Extinction coefficient, 102
Extra-nuclear structure, 591

F

Faraday, 361
Ferments, 353
Filters, 547
First order reactions, 330
Fluidity, 58
Fluorescence, 543
Formaldehyde production, 352

Formula (see also *equation, law*)
Formula of Debye (specific heat), 106
of Gibbs (surface concentration), 236
of Laplace (velocity of sound), 28
of Lorenz and Lorentz (refractive index), 92
of Planck (radiation), 600
of Rayleigh (radiation), 541
of Wien (radiation), 541
Franck energy diagram, 619
Free energy, 131, 435, 506
equations, addition of, 506
from equilibrium constants, 507
of N_2O_4 dissociation, 507
and temperature, 508
and chemical reactions, 271
Freezing-point apparatus, Adams', 178
constants, 175
depressions, 194
determination, 177
lowering, 174
Frequency of light, 99
Fugacity, 273, 511
Fundamental series, 605

G

Gamma (γ), 448, 449
Gamma-rays, 538, 575
Galvanic cell, 431
Gas, 9
collisions in, 342
constant, molar, 10
degree of dissociation of, 20
density, 14
effusion of, 25
expansion, 122
heat capacities of, 30
ions, 556
internal energy of, 114
kinetic theory of, 339
laws, 9
laws, accuracy, 36
laws, deviations from, 11
limiting density for, 39
liquefaction of, 40
perfect, 11
physical constants of, 43
solubility of, 141
specific heat of, 26
Gay-Lussac-Joule experiment, 115
Gelation, 209
Gels, 233
properties of, 235
Glass electrode, 475
Gold number, 225
Gram-equivalent, 364

H

Haber process, 351
Half-life period, 332, 578
Heat capacity, 113
capacity at low temperatures, 81
capacity of silver, 525
capacity of solids, 81
of combustion, 258
content, 113
of dilution, 253
of dissociation, 262
of formation, 250
of formation of ions, 264
of hydration, 253
of ionization, 263
of neutralization, 261
of reaction, variation with temperature, 257
of solution, 252
of solution, integral, 253
of vaporization, Mathews apparatus, 171
Helium, 43
Helmholtz double layer, 444
Hertzian waves, 538
Heterogeneous equilibrium, 288
equilibrium and temperature, 295
systems, 288
Heteropolar bond, 595
Hohlraum, 539
Homogeneous equilibrium, 267
Homopolar bond, 596
Hydrogel, 209
Hydrogen electrode, 459, 460
electrode, formula for, 462
electrode titrations, 465
ions, 463
ion concentrations, 463
ions, electrodes for measuring, 473
Hydrolysis, 400, 405, 410
determination by conductance, 394

Hydrolysis, electrometric determination of, 472
of salt of a strong base and a weak acid, 412
of salt of weak base and strong acid, 413
of salt of weak base and weak acid, 413
Hydrolytic constant, 473
Hydrophile, 210
Hydrophobe, 210
Hydrosol, 209
Hypothesis, 1
of Prout, 3, 566

I

i, 194
Ideal solutions, 145
Immiscible liquids, 153
Increment, 109
Index of refraction, 89
Indicator constant, 417
Indicators, 471
Induction period, 549
Infra-red, 528
Integral, 109
Intensity factor, 110
Interionic attraction, 410
attraction theory, 199, 478
Intermediate compounds in kinetics, 349
Internal energy, 112
Intrinsic energy, 110
Inversion of cane sugar, 330
Ion product of water, 464
Ionic atmosphere, 480
strength, 200, 480, 517
velocities, measurement of, 385
Ionization and activity, 448
of acetic acid, 401
chamber, 73
constants of acids, 402
constants of bases, 403
constants, benzoic acid derivatives, 404
constants, carbonic acid, 401
constants, propionic acid derivatives, 404
constants, substituted acetic acids, 403
constant, of water, 414
influence of substitution, 403
Ionization potentials, 609
of water, 415
Ionized solutes, completely, 197
Ionizing power of solvents, 391
Ions, 364
electrolytic, 363
gas, 363
migration of, 366
Irreversible cell, 493
Isobars, 584
Isoelectric point, 224
Isomorphism, 3
Isosteres, 598
Isothermal expansion, 121
Isotopes, 5, 565, 567, 584
Isotropic, 65

J

Joule, 245, 362
Joule-Thomson effect, 116
Junction, flowing, 455
potentials, 452
potentials, correction for, 455

K

K, 270
k, 323
Kilowatt-hour, 362
Kinetic energy, 110
equation deductions, 23
equation, derivation of, 22
theory of gases, 22, 28, 339
Kinetics, 321
of complex reactions, 332
photochemical, 548
temperature coefficient, 345

L

Lattice, body-centered, 70
face-centered, 70
simple cubic, 70
of sodium chloride, 75
Law (see also *formula*, *equation*)
Law of Avogadro (gases), 3
of Beer (absorption of light), 544
of Boyle (gases), 9
of Cailletet and Mathias (densities), 48
of Dalton (partial pressures), 139, 294

Law, of Dulong and Petit (atomic heats), 3, 82
of Einstein (photochemistry), 545, 551
of Faraday (electrolysis), 363, 364, 421
of Fajans and Soddy (radioelements), 583
of Fresnel (reflection), 544
of Gay-Lussac (gases), 9
of Graham (gas diffusion), 25
of Grotthus (photochemistry), 545
of heat summation, 248
of Henry (gaseous solute), 141, 145, 163, 294, 512
of Kohlrausch (ionic conductance), 378
of Kopp (molar volumes), 87
of Kirchhoff (absorption of light), 540
of Lambert (absorption of light), 543
of Lavoisier and Laplace (thermochemistry), 248
of mass action, 268
of Maxwell (distribution), 340
of Moseley (atomic numbers), 568
of Ostwald (dilution), 400
of photochemistry, 545
of radiation, 540
of Ramsay and Young (vapor pressure), 50
of Raoult (vapor pressure solvent), 162, 163
of Stefan-Boltzmann (radiation), 540
of Trouton (heat of vaporization), 51
Lead storage cell, theory of, 498
storage cell, maintenance of, 497, 498
Light, different types, 538
absorption, measurement of, 99
Liquefaction of gases, 40
of gases, principles involved, 42
Liquid crystals, 84
pairs, 143
Liquids, 33
associated, 52
internal pressure of, 52
partially miscible, 153
viscosity of, 57
ln x, 109
log x, 109
Luminescence, 542
Lyman series, 603
Lyophile, 210
Lyophilic colloids, 230
Lyophobe, 210
Lyophobic colloids, 230

M

Manometer, of Rayleigh, 165
Mass spectrograph, 564, 565
spectrum, 564
Maxima and minima, 152
Maximum boiling-points, 151
work, 121
Melting-point, change, 129
Membrane, nature of, 182
Metastable melting-point, 301
solution, 156
Methanol synthesis, 353
Method of intercepts, 532
Mercurous ion, 459
Mercury vapor, activated, 551
Micron (μ), 99, 208
Miller indices, 64
Millimicron ($m\mu$), 99, 208, 602
Mitogenetic rays, 553
Molal solution, 138
volumes of methanol and water, 532
Molar solution, 138
volume, 86, 88
Molecular constitution, 86
diameters, 343
weight, 14
weight, Lumsden method, 18
weight, Regnault method, 15
weight, Victor Meyer method, 16
Molecules, 2
Mol fractions, 138
Monochromator, 547
Mu (μ), 200, 208, 480, 517
Mutations, 553

N

Nernst's constants, 528
Nickel oxide storage cell, 499
plating, 496
Normal electrode potentials, 441, 442
Nuclear theory of atoms, 588

O

Odd molecules, 599
Ohm, 361

Optical activity and chemical constitution, 96
anomaly, 93
isomers, 96
Order of reaction, determination of, 331
Orientation at interface, 233
Ortho and para hydrogen, 620
Osmosis, 180
mechanism of, 181
Osmotic apparatus of Frazer and Myrick, 188
apparatus of Berkeley and Hartley, 185
coefficient, 478
pressure, 167, 182
pressure measurement, 184
properties of electrolytes, 201
Overvoltage, 494
Oxidation, 436
potentials, 436
Ozone, 547

P

Packing effect, 590
fraction, 591
Parachor of Sugden, 89
Partial differential, 109
molal quantities, 530
Paschen series, 603
Passivity, 493
Pauli's exclusion principle, 606
Perfect radiator, 539
Periodic table, 593
Planck's constant, 6, 542, 601, 611
Plastic flow, 59
Plasticity, 59
*p*H, 463
*p*H of acids and bases, 464
Phase, 288
Phase rule, 297
Phosphorescence, 543
Photo-bromination of cinnamic acid, 550
Photochemistry, 538
experimental technique, 547
temperature effect, 550
Photoelectric effect, 610
Photography, 551
Photosensitization, 551
Physical chemistry, survey of, 7
Physical properties, 86
properties and valence type, 597
Poggendorf compensation method, 422
p OH, 464
Poise, 57
Poisons, catalyst, 350
Polar and non-polar compounds, 52
Polar compounds, 592
Polarimeter, 94
Polarity of molecule, 107
Polarization, 487, 488
apparatus for the measurement of, 498
capacity, 489
measurement, 489
Polarized light, rotation of, 94
Polarizing microscopes, 66
Polymerization of anthracene, 549
Polymerized solute, 294
Polymorphism, 67
Positive rays, 563
Potential energy, 110
Potentials, ferri-ferro, 439
ferric-stannous, 437
ferrous-mercuric, 440
Potentiometer, 423, 424
voltmeter, 465
Potentiometric titrations, 466, 475
titrations, oxidation reduction, 474
titrations, magnesium hydroxide, 469
titrations, precipitations, 476
Powder method of X-ray analysis, 77
Precipitation, mutual, 226
Pre-dissociation, 615
Principal series, 605
Promoters, 350
Protective colloids, 224
Proton, 6, 588
theory of acids and bases, 405

Q

Quantum, 2, 6, 542, 600
collisions, 614
efficiency, 545
mechanics, 619
numbers, 605
numbers, principal, 606
theory, 542, 600, 601
Quinhydrone electrode, 473

R

Radiant energy, 538
Radiation, energy of, 546
  frequency of, 546
  hypothesis, 346
  nature of, 573
  ways of expressing, 602
Radioelements and periodic table, 581
  disintegration series, 580
Radio indicators, 584
Radioactive constant, 575
  disintegration, 576
  equilibrium, 577
Radioactivity, 572
  application of, 585
  discovery of, 572
  measurements of, 574
Radioluminescence, 543
Radium, 573
Radon, 575
Raman effect, 612
Reaction isochore, 284
  mechanisms, 585
  at constant pressure, 254
  at constant volume, 254
Reduction, 436
  potentials, 436
  potentials, normal, 440
Reflection, 543
Refraction, atomic, 93
  molar, 91
  specific, 91
Refractive index of liquids, 89
Refractometer, 91
  of Pulfrich, 90
Residual current, 490
Resistance, electrical, 363
Resonance potential, 609
Reversible cell, 493
  cycles, 119
Rickets, 553
Rotation, magnetic, 97
  molar, 95
  specific, 95
Rule of Schulze-Hardy (colloids), 223
Rule of Thornton (thermochemistry), 259
Rydberg constant, 602, 604

S

Sabatier's dehydrogenation process, 352
  hydrogenation process, 351
Salting-out effect, 142
Saponification, ethyl acetate, 328
  ethyl succinate, 335
  methyl acetate, 328
Saturated, 155
  solution, 140
Saturation current, 574
Schrödinger wave equation, 619
Second order reactions, 326
Sedimentation equilibrium, 212
Semi-permeable, 140
  membrane, 180
Separation values of ions, 496
Sharp series, 605
Side reactions, 334
Signs in electrochemistry, 432
Solation, 209
Solids, 62
Solubility, thallous chloride, 409
  curves, 157
  of difficultly soluble salts, 393
  of gases, 141
  product, 407, 408, 409
  product silver bromate, 408
  product in concentrated solutions, 409
  of silver chloride, 459
Solute, 137
Solutes, abnormal, 193
Solutions, 137
  comparison of methods, 188
  composition of, 137
  concentrated, 202, 205
  consolute, 137
  dilute, 162
  of gases, 139
  of gases in liquids, 140
  liquid, 308
  saturated, 155
  solid, 158, 308
  of solids in liquids, 155
  of succinic acid, 296
  thermodynamic relations, 188
Solvates, 202
Solvent, 137
Specific conductance, 375
  heats at constant volume, 83

Specific heats, ratio of, 27
heats of liquids, 256
heat, Kundt's method, 28
heats, relation between, 118
heat, variation with temperature, 255
reaction rate, 325
Spectra, rotation-vibration, 617
Spectrograph quartz, 101
Spectrophotometer, 103
Spectrophotometry, 102
Spectroscopy, 601
Spectrum, absorption, 615
of hydrogen, 603
Standard state, 512
cell, 425
Steady state, 354, 579
Stokes lines, 613
Storage cells, 497
Strength of acids and bases, 401
Sublimation curve, 299
Supersaturated solutions, 156
Surface concentration, 236
tension, 53
tension, drop weight method, 56
tension and temperature, 55
System aniline-sulphur dioxide, 320
chloroform, water, acetic-acid, 311
copper-manganese, 320
d- and *l*-carvoxime, 309
ferric chloride and water, 306
gold-aluminum, 317
$HgBr_2$-HCl_2, 310
HgCl-NaCl, 308
KNO_3-$TlNO_3$, 310
phenol and water, 143
potassium chloride and water, 303
solutes in liquid solvents, 303
sulphur, liquid-vapor, 300
two-component, 302
water-aniline-phenol, 312
water-ice-vapor, 297
water-ether-succinic nitrile, 313
zinc-cadmium, 314

T

Temperature coefficient of reaction rates, 336
Termolecular reactions, 329, 331
Theorem of Le Chatelier, 133, 151
Theory (see also *law, equation*)
Theory of Arrhenius (electrolytic dissociation), 195, 381
of Brönsted (acids), 354
of Debye-Hückel (interionic attraction), 199, 477
of emulsification, 232
of gases, kinetic, 339
of indicators, 416
interionic attraction, 478
quantum, 600
Thermal analysis, 313
Thermochemical equations, 245, 249
measurements, 246
Thermochemistry, 245
allotropic forms, 260
Themodynamics, chemical, 506
elementary principles, 109
first law, 111
second law, 123
third law, 524
Thermoluminescence, 542
Thermometer, Beckmann, 177
Thermoneutrality of salt solutions, 260
Thermopile, 547
Three component systems, 310
Tie-line, 312
Titration of acetic acid, 467
of acids and bases, 466
differential, 477
oxidation-reduction, 476
of sodium carbonate, 468
Transference numbers, 367
numbers of cations, 371
numbers, electrometric determination of, 456
numbers, experimental determination, 369
numbers of hydrochloric acid, 367
numbers and ionic hydration, 370
numbers of lithium ion, 457
numbers of silver nitrate, 369
Transition-point, 300
Transition temperature, 67
Transmutation, 588
Transport numbers, 367
Triangular diagram, 310
Triboluminescence, 543
Tyndall phenomenon, 210

U

Ultracentrifuge, 218
Ultrafiltration, 211
Ultramicroscope, 210
Ultraviolet, 538
Uncertainty principle, 612
Unimolecular reaction, 331
  reaction, experimental data, 323
  reaction, mathematical treatment of, 322
  reaction, mechanism of, 346
  reactions, pseudo-unimolecular, 330
Uranyl oxalate, 548

V

Valence, 595
Vapor densities, abnormal, 19
Vapor density determinations, 18
  pressure, air-saturation method, 167
  pressure of binary mixtures, 147
  pressure, dynamic method, 167
  pressure, Frazer and Lovelace method, 165
  pressure and heat of vaporization, 130
  pressure of liquids, 45
  pressure lowering, 162
  pressure, measurement of, 47, 164
  pressure and temperature, 46
Vaporization, heat of, 50
Velocities of complex reactions, 333
Velocity constant, 323
  of colloids, 220
  of gaseous molecule, 26
  of ions, absolute, 383, 385, 387
Viscometer, 58
Viscosity of colloids, 217
  of liquids, 57
  of strong electrolytes, 480
Viscous flow, 59
Vitamin D, 552
Volt, 361, 610
Volt-ampere, 362

W

Watt, 362
Wave-numbers, 99
Welsbach mantle, 353
Wheatstone bridge, 373

X

X-rays, 538
  analysis, and atomic numbers, 568
  analysis, Bragg method, 71
  analysis, Debye-Scherrer method, 77
  analysis, Hull method, 77
  applications, 79
  and crystal structure, 67
  spectrometer, 73
  wave-lengths, 76

Z

Zeolites, 159
Zero order reaction, 350
Zinc amalgams, E.M.F., 446
Zinc electrode, 433
Zinc-copper cell, 434